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AN APPROXIMATE *AB INITIO* MOLECULAR ORBITAL THEORY

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GLOSSARY OF TERMS

AO - abbreviation for atomic orbital. An AO is not necessarily orthogonal to all other AO's in a molecule.

ab initio - "from first principles." This title is usually used to distinguish methods which do not use empirical or semi-empirical methods, i.e. methods which spring directly from the theory.

Adiabatic ionization - an ionization the initial state of which is the equilibrium geometric configuration of the neutral molecule and the final state of which is the equilibrium configuration of the ion.

"Best atom" atomic orbital - A Slater type atomic orbital the orbital exponent of which is determined variationally for the isolated atom using a minimum set of atomic functions.

CNDO - abbreviation for complete neglect of differential overlap. All integrals over atomic overlap-density functions are neglected in the calculation.

Correlation - Generally correlation effects are defined as those effects not accounted for by the Hartree-Fock orbital theory. The motion of the electrons is correlated in the statistical sense.

GSOAO - abbreviation for Gram-Schmidt orthogonalized atomic orbital. These functions are not "symmetric."

Gaussian atomic function - an approximation to a Slater type atomic orbital. A Gaussian function has $\exp(-\alpha r^2)$ dependence instead of the $\exp(-\xi r)$ dependence of STO's.

HOMO - abbreviation for highest occupied molecular orbital.

INDO - abbreviation for intermediate neglect of differential overlap. In this method, all overlap integrals are neglected and most, but not all, energy-integrals over atomic overlap-charge densities.

LCAO-MO - abbreviation for linear combination of atomic orbitals-molecular orbital. A molecular orbital is approximated by a sum of atomic orbitals.

LOAO - abbreviation for Löwdin orthogonalized atomic orbital. These functions are "symmetric."

MINDO - abbreviation for modified intermediate neglect of differential overlap. This is essentially an INDO method with a different parameterization.

MO - abbreviation for molecular orbital.

NDDO - abbreviation for neglect of diatomic differential overlap. This is the same formalism as CNDO except that only integrals which involve multi-center atomic overlap density functions are neglected.

NDO - abbreviation for neglect of differential overlap. This is any formalism where overlap is neglected and some energy-integrals over atomic overlap-density functions are neglected.

OAO - abbreviation for orthogonalized atomic orbital. The orbitals of the set {i} are orthogonal if and only if the inner-product $(i|j) = \delta_{ij}$ (δ_{ij} is the Kronecker delta).

Orbital exponent - The ξ term which appears in the exponential part of a STO, i.e. $\exp(-\xi r)$. ξ is the effective nuclear charge divided by the principal quantum number of the STO. The larger ξ the smaller is the relative size of the AO.

PNDO - abbreviation for partial neglect of differential overlap.

SCF - abbreviation for self-consistent field. An iteration method for solving some of the secular equations which appear in atomic and molecular problems.

STO - abbreviation for Slater-type orbital. These are single-term approximations to SCF-AO's. The radial factors for STO's are not always orthogonal, i.e. some orbitals of the same symmetry type but different principal quantum number have non-zero overlap.

VB - abbreviation for valence-bond. A method for building molecular wave functions as products of atomic orbitals rather than from molecular orbitals.

Variational method - A method for finding approximate solutions to eigenvalue differential equations.

If $Lu_i(x) = \lambda_i u_i(x)$, then a trial solution $\Phi(x)$ obeys the variational principle,

$$W_\Phi = (\Phi|L|\Phi)/(\Phi|\Phi) \geq \lambda_0,$$

where λ_0 is the lowest of the eigenvalues.

Vertical ionization - an ionization which does not involve a change in the geometry of the neutral molecule. The final state of the ionization is the ion in a non-equilibrium geometric configuration.

ZDO - abbreviation for zero differential overlap. This is an early form of CNDO which was applied to π-electron systems.

AN APPROXIMATE *AB INITIO* MOLECULAR ORBITAL THEORY

CHAPTER I

INTRODUCTION

Several years ago it was noted by a quantum chemist that the workers in the area of molecular quantum mechanics could be classified into two areas. These areas were (1) the researchers working on large molecules using semi-empirical approaches and (2) the researchers doing *ab initio* calculations on small molecules. This scientist concluded that what was needed was a contingent of workers in the middle ground, people who could extend the *ab initio* methods successfully to large molecules.

Although today one finds primarily the same two-area division, the years following this publication have seen a few advances toward this goal. One such advance is the increased use of Gaussian atomic functions as the basis for the expansion of the molecular orbitals. Although the Gaussian expansions converge slowly (many Gaussians are needed in the calculations), the integrals over Gaussians are relatively easy to do, and the computation time with these functions is less than with a Slater-type atomic orbital calculation to roughly the same accuracy. All-electron calculations on molecules of benzene-size and larger are possible with these techniques.[1-3] Another area in which some progress has been made towards that author's goal is that of providing a theoretical basis

for the approximations used in the semi-empirical methods. The material in this dissertation falls into this last category.

Even in 1971, it is safe to say that most researchers who are applying molecular orbital calculations use the Hückel[4] method or the Pariser-Parr-Pople SCF method[5,6] for π-electron studies. For all-electron (σ-orbitals also) calculations, most researchers would select the CNDO/2 method of Pople, Santry, and Segal,[7-10] the CNDO/2 method with the Del Bene-Jaffé[11,12] parameterization for ultra-violet spectra, the MINDO/2[13,14] method of Dewar, or perhaps the extended Hückel method.[15] These are all semi-empirical procedures. (I do not intend to discuss the above methods here as excellent reviews are available.)[4,16,17]

These procedures have all been developed in a partially intuitive manner, and many quantum chemists have felt it worthwhile to try to provide better theoretical justification for the methods. Indeed, one obstacle to wider use of the methods is a mistrust generated by the lack of a convincing justification.

In this chapter, some of the efforts to justify the semi-empirical methods will be briefly reviewed and the research effort presented in this dissertation will be placed in the context of these efforts. Since neglect of differential overlap (NDO) semi-empirical theories are in the majority of those used, only efforts made to justify theories of this type are discussed. (These NDO theories assume that all overlaps between atomic orbitals are zero and that many or all of the electron-repulsion integrals involving overlap-charges are zero.) The material in subsequent chapters is also generally restricted to the neglect of

differential overlap approximations.

Serious efforts to provide a theoretical basis for the neglect of differential overlap methods began shortly after Pariser and Parr proposed[5] the zero differential overlap approximation (ZDO) for π-electron calculations. These efforts invoked the atomic orbitals generated by the Löwdin method[18] of symmetrically orthogonalizing functions as the orbital basis of the ZDO approximation. In the Löwdin procedure, the orthogonalized atomic orbitals (OAO's) are obtained by a transformation

$$\phi = \Phi \underset{\sim}{S}^{-\frac{1}{2}}, \tag{1}$$

where ϕ is the row matrix with each element a Löwdin orthogonalized atomic orbital (LOAO), Φ is the row matrix with each element an atomic orbital (AO), and $\underset{\sim}{S}$ is the overlap or metric matrix of the AO's. The LOAO's are symmetrically orthogonal. That is, where the MO's of a molecule are determined by symmetry, the expansion of MO's in LOAO's produces a set of expansion coefficients (within a normalization factor) the same as the set of coefficients in an AO expansion.

With LOAO's, the matrix form of the Roothaan secular equations for AO's is reduced from

$$\underset{\sim}{H}\,\underset{\sim}{x} = \underset{\sim}{S}\,\underset{\sim}{x}\,\underset{\sim}{E} \tag{2}$$

to the form

$$\underset{\sim}{H'}\underset{\sim}{C} = \underset{\sim}{C}\,\underset{\sim}{E}\ . \tag{3}$$

In these equations, $\underset{\sim}{H}$ is the matrix which collects the elements $H_{\mu\nu} = \int \Phi_\mu^* H_{op} \Phi_\nu d\tau$, where H_{op} is the one-electron Hartree-Fock operator. $\underset{\sim}{E}$ is the diagonal matrix of the MO energies, and $\underset{\sim}{x}$ and $\underset{\sim}{C}$ are the matrices of the MO expansion coefficients of AO's and LOAO's respectively. The matrix $\underset{\sim}{H'}$ is related to $\underset{\sim}{H}$ by the transformation

$$\underset{\sim}{H}' = \underset{\sim}{S}^{-\frac{1}{2}} \underset{\sim}{H} \underset{\sim}{S}^{-\frac{1}{2}}. \qquad (4)$$

It is difficult to say who first realized that the LOAO's justified the ZDO approximations of π-electron theory. Probably it was Löwdin himself, and this fact was apparently indicated to Parr in a private communication.[19] The first proof of the ZDO assumptions to appear in print was that of Fumi and Parr,[19] who rationalized ZDO by LOAO's for diatomic π-electron systems. About this same time, McWeeny[20,21] was employing LOAO's to do valence-bond calculations. However, the usefulness of LOAO's for VB calculations is more restricted than for MO methods. A very complete discussion of the importance of LOAO's in rationalizing the ZDO approximation has been given by Parr.[22]

More recently, Fischer-Hjalmars[23] extended the results of Fumi and Parr to general polyatomic systems. It is interesting that her efforts, unlike the efforts of Fumi and Parr (1) were applied not only to two-electron integrals (electron repulsions), but also to the α and β integrals, and (2) had as an essential feature in the mathematical proofs the assumption of the validity of the Mulliken approximation for AO integrals.[24] This approximation may be generally written as

$$ab = \frac{1}{2} S_{ab}(aa + bb), \qquad (5)$$

where ab is an overlap-density function for the AO's a and b, and aa and bb are the atomic density functions. To approximate integrals involving overlap-densities, one inserts this approximation for ab into the particular integral. It should be pointed out that the validity of the Mulliken approximation is essential to the proofs. The proofs are as accurate as the Mulliken approximation is valid. The assumption of its validity for one-electron integrals (α's and β's) leads to some unacceptable consequences.

For example, if the Mulliken approximation is valid for one-electron integrals, then resonance integrals (β's) calculated over LOAO's for diatomic π-electron systems are zero. The fact that LOAO's rationalize the neglect of certain two-electron integrals in the ZDO approximation is due entirely to the Mulliken approximation being a good one for two-electron integrals. Needless to say, Fischer-Hjalmars did not fully apply the Mulliken approximation in the calculation of one-electron integrals over LOAO's. She did, however, use this approximation to estimate some of the terms which were factors of S^2 and higher order in overlap in the binomial series[18] expansion of α and β. She came to the conclusion that since one could represent β_{ij}^{LOAO} as

$$\beta_{ij}^{LOAO} = \beta_{ij}^{AO} - \frac{1}{2} S_{ij}\{\alpha_i^{AO} + \alpha_j^{AO}\} + O(S^3), \qquad (6)$$

that β_{ij}^{LOAO} is transferable from one molecule to another. The conclusions in this dissertation will disagree strongly with Fischer-Hjalmars' conclusions. The use of the Mulliken approximation to estimate one-electron integrals is not valid. The use of the slowly convergent binomial expansion also leads to errors. The discussion in chapter VI shows that, even for a two-atom π-electron system, the first two terms in the expansion should be multiplied by a factor containing a term of the order of S^2.

A series of papers developing and applying a semi-empirical π-electron MO theory based upon Fischer-Hjalmars' conclusions has appeared.[25-29] The only real improvement over the original Pariser-Parr-Pople procedure was the recognition that α's were somehow overlap-coupled to their neighbors. The electronic transition energies calculated with this method are better than with the original Pariser-Parr-Pople method.

It was at this point that the work represented in this dissertation

really began. I could not help but feel that the accuracy in the Mulliken approximation was, in fact, the critical point, particularly in the case of one-electron integrals. Since no one had used the LOAO's to derive a set of uncomplicated, usable equations for one-electron integrals in MO calculations, and since these terms were treated intuitively in the semi-empirical MO theories, I wondered if uncomplicated equations for the one-electron integrals could be derived from LOAO's. The intuitive equations for β's in NDO theories were all based on β_{ij} being a linear function of the overlap S_{ij}. Was this really the case? If so, then under what conditions? Obviously, the derivations of α and β could not assume the validity of the Mulliken approximation.

One of the fundamental problems involved in the undertaking outlined in the previous paragraph is the generation of the LOAO's. Obtaining the transformation matrix $\underset{\sim}{S}^{-\frac{1}{2}}$ is not a trivial procedure. Löwdin[18] originally suggested using a binomial expansion of $(\underset{\sim}{1} + \underset{\sim}{S}')^{-\frac{1}{2}}$, where $\underset{\sim}{S} = \underset{\sim}{1} + \underset{\sim}{S}'$. This leads to the equation

$$(\underset{\sim}{1} + \underset{\sim}{S}')^{-\frac{1}{2}} = \underset{\sim}{1} - \frac{1}{2}\underset{\sim}{S}' + \frac{3}{8}\underset{\sim}{S}'^{2} - \frac{5}{16}\underset{\sim}{S}'^{3} + \ldots . \qquad (7)$$

The expansion produces the following general form for a LOAO:

$$\phi_\mu = \Phi_\mu - \frac{1}{2}\sum_\alpha \Phi_\alpha S_{\alpha\mu} + \frac{3}{8}\sum_{\alpha\beta} \Phi_\alpha S_{\alpha\beta} S_{\beta\mu} - \ldots . \qquad (8)$$

Although this is an infinite series and difficult to handle mathematically, this is the form for LOAO's used by Fumi and Parr and Fischer-Hjalmars in their derivations. The series is slowly convergent for the overlaps found in molecules, and this fact prevents serious derivations with it.

Löwdin found that LOAO's could be generated in closed-form for

systems with cyclic S-matrices[30] (S-matrices where succeeding rows of the matrix may be generated from the first row by cyclic permutation of the elements of the first row). Such systems would include the π-systems of ethylene, benzene and cyclobutadiene. Use of these closed-form solutions limits one to a very restricted class of molecules, however.

The difficulties inherent in the binomial expansion technique led Löwdin and co-workers to try a new method.[31,32] This method is that used to compute a function of a symmetric matrix. If

$$\underset{\sim}{U}^{\dagger}\underset{\sim}{S}\,\underset{\sim}{U} = \underset{\sim}{D} \qquad \text{(D is a diagonal matrix)} \tag{9}$$

then, if $\underset{\sim}{S}$ is symmetric ($\underset{\sim}{S}$-transpose = $\underset{\sim}{S}$)

$$f(\underset{\sim}{S}) = \underset{\sim}{U}\, f(\underset{\sim}{D})\, \underset{\sim}{U}^{\dagger}. \tag{10}$$

$\underset{\sim}{U}^{\dagger}$ is $\underset{\sim}{U}$-adjoint (the complex conjugate of $\underset{\sim}{U}$-transpose). The object is to calculate $f(\underset{\sim}{S}) = \underset{\sim}{S}^{-\frac{1}{2}}$. This technique has been applied in the orthogonalization of functions for solids. However, obtaining $\underset{\sim}{S}^{-\frac{1}{2}}$ by this method involves complicated numerical techniques.[33] The method does not produce forms for LOAO's which are manageable in mathematical derivations, and closed-forms are apparently still restricted to cyclic systems.[33]

One would prefer to have a more convenient method for generating LOAO's than those methods discussed previously. One might even sacrifice some accuracy in order to have manageable approximate equations for LOAO's. Chapter III of this dissertation is concerned, at least in part, with the development of a method to produce and test such a set of approximate equations.

More recently, semi-empirical methods have been extended to σ-electrons. The approximations inherent in ZDO were brought over to

all-electron calculations and renamed CNDO[7] (complete neglect of differential overlap), NDDO[7] (neglect of diatomic differential overlap), INDO[34] (intermediate neglect of differential overlap), MINDO[13] (modified intermediate neglect of differential overlap), or PNDO[35] (partial neglect of differential overlap). These are all various levels of approximation along the lines of the original ZDO approximation. Dewar's excellent book should be consulted for details.

These NDO (all the abbreviations have at least this much in common) methods have invoked the LOAO's as the orbital basis for the approximations that have been made. Relatively recent studies of several small molecules (H_2O, CH_4, C_2H_6, C_2H_4, H_2CO, etc.) in a LOAO basis by Cook, Hollis and McWeeny[36] and by Cook and McWeeny[37] have helped to show how far the LOAO basis can be used to rationalize the NDO approximations. The authors of these papers have shown that at least an INDO formalism is necessary to obtain good charge densities in molecules. Their calculations also served to provide comparisons of LOAO-calculated α's and β's to parameterized values. The studies were done accurately, with no integral approximations and with fairly accurate LOAO's (binomial expansion method). The studies are useful as studies but good, uncomplicated approximate expressions for α's and β's were not derived (see Chapter VI).

An entirely different approach to the problem of calculating α's and β's for the Pariser-Parr-Pople method and for the various NDO theories is that developed by Linderberg[38] and extended by Wratten.[39] From the equivalence of the dipole length and velocity forms of the oscillator

strength (Heisenberg equation of motion), Linderberg deduced a dependence of $\beta_{\mu\nu}$ upon the overlap $S_{\mu\nu}$ in the form of the equation

$$\beta_{\mu\nu} = \frac{1}{R_{\mu\nu}} \frac{d\, S_{\mu\nu}}{d\, R_{\mu\nu}}, \tag{11}$$

where $S_{\mu\nu}$ is the overlap of the AO's and $R_{\mu\nu}$ is the internuclear distance. β's were calculated for the π-electron systems of benzene and ethylene with this method and the results agreed with the original Pariser-Parr parameterization. Wratten applied the method to the calculation of β's for σ-AO's.

The Linderberg derivation had the anomoly that a β over orthogonal functions should be proportional to the derivative of the overlap of AO's. This anomoly was removed by Jug[40] who explicitly used LOAO's in the development of the above equation. He also used the method to obtain approximate equations for α.

I have a feeling that something is wrong with these derivations. A conversation with Jug at the 1971 Sanibel symposium revealed that the use of the equation was producing some strange results. A test of this equation for the H_2 molecule is included in Chapter VI. The results of this test are interesting.

The original purpose of the work presented in this dissertation was to develop an *ab initio* approximation to accurate *ab initio* all-electron calculations. This approximation was to embody as many of the approximations of the NDO formalism as were found to be accurate for an actual LOAO basis. It was planned that the approximate *ab initio* MO theory would be about as easy-to-use a procedure as the NDO semi-empirical methods. This goal was achieved, but only for π-electron theory. Certain obstacles arose (notably the generation of the LOAO's) which limited

the effort to π-electrons only.

Using this theoretical method for π-electrons, it was possible to check some aspects of the semi-empirical procedures by comparing the calculated values for integrals to the parameterized values. The method was also used to calulate π-electron properties of molecules, and the calculated ionization potentials and electronic transitions were compared to experiment. One wonders how far the semi-empirical parameterization was going towards obtaining actual integrals over LOAO's, and how far the parameterization was going towards including effects which lie, in reality, outside orbital theories (electron-correlation effects). The comparison of the calculated results of the approximate *ab initio* method to experiment should help to answer this question. The effort represented by this dissertation has served to (1) point up some of the defects in the NDO semi-empirical methods and (2) to suggest better approximations. Some alternatives to the NDO parameterizations have been suggested to include effects outside the simple orbital theory developed here.

In the chapters which follow, the LOAO basis is discussed, and its advantages and disadvantages in representing a molecular wave function are pointed out. A method is proposed for approximately obtaining LOAO's for π-electron systems. The method is thoroughly tested. In this chapter (Chapter III), a transformation theory of the Gram-Schmidt orthogonalization procedure is presented. In the past, the Gram-Schmidt procedure has been given in the form of an algorithm, and this does not allow one to write Gram-Schmidt orbitals directly in terms of the overlapping orbital set. Löwdin also realized this problem and, in a recent

publication,[33] has shown a method alternative to that in Chapter III. It is felt that the method presented in this dissertation is more rigorous and mathematically "neater" than that of Löwdin.

Chapter IV presents the derivation of the approximate *ab initio* MO theory. In this chapter, the development appears in a very detailed form. However, due to the great number of approximations developed, the final equations, which are to be employed in actual calculations with the method, are relatively uncomplicated.

Chapter V evaluates the results of calculations using the method derived in Chapter IV. These calculations were done using an SCF program, the self-consistency check being on the bond-order matrix. The resulting charge densities, ionization potentials, and electronic spectra were all evaluated in light of more accurate calculations or of experimental data.

Chapter VI presents a discussion of the "one-electron" parameters of several semi-empirical theories. The semi-empirical parameters are compared to the "one-electron" integrals actually calculated in the present work. This chapter establishes a better basis for the NDO procedures where such procedures are found to be correct and points out corrections to the procedures where they are in error.

The last chapter of this dissertation discusses a modification of the SCF method to give an "independent particle" or Hückel procedure. For several small molecules (H_2, HeH^+, and LiH), the NDO SCF formalism is compared to an *ab initio* Hückel method. This *ab initio* method displays the "insides" of the Hückel α and β integrals, which are always parameterized. Although an extension of this approach to larger and more interesting molecules was attempted, several, at present insurmountable,

problems in such an extension became apparent. These problems are discussed.

Such an "independent particle" theory is *ad hoc*. It does not spring directly from first principles but is designed to give total electronic energies and to give electronic transition energies with less computational difficulty than SCF approximations to Hartree-Fock. At the same time, however, such a theory does not give ionization potentials as the negative of the orbital energies.

Discussions of Hückel theory for π-electron systems may be found in the books of Streitwieser or Dewar. The newer extended Hückel theory (extended to σ-electrons) is discussed in Dewar's book. A brief discussion in Dewar's book* is the only one that I have found which is anything like that found in Chapter VII.

The purpose of the work presented in this chapter is to elucidate, via reasonably rigorous techniques, the problems involved in developing an "independent particle" approach. In light of the failures of the extended Hückel treatments, such an investigation appears to be in order. Such an investigation should suggest some ways to improve the Hückel theory.

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* Page 92 of reference 16.

CHAPTER II

ESTABLISHING AN ATOMIC ORBITAL BASIS

In NDO theories, it is generally assumed that LOAO's form the atomic basis for LCAO-MO expansions. Why use LOAO's? Why not use another orthogonal set? There are as many sets of n orthogonal functions as there are n x n unitary matrices (see Chapter III for details). Why, indeed, use orthogonal functions at all?

One would like to choose a basis set of atomic functions which allows as much simplification of the mathematics of the calculation of molecular properties as possible. This simplification can be through exact mathematical means or through simplification of the arithmetic via a set of adequate approximations. LOAO's provide a maximum amount of both types.

Since they are orthogonal functions, the LOAO's reduce the Roothaan equations for the expansion coefficients of a set of AO's to a set of secular equations. This reduction is exact. But then any set of OAO's will provide this simplification.

The LOAO's allow one to assume that certain of the electron-repulsion integrals encountered in SCF-MO calculations are zero. These are integrals involving atomic density functions formed by the overlapping of two LOAO's. This approximation is best or at least very nearly best for LOAO's. It has been found that LOAO's are very nearly those

functions which minimize the exchange integrals $(ab|ab)$.[41,42] However, these integrals are decreased from their values over atomic functions by the requirement that a and b be simply OAO's. An example for the π-electron system of ethylene is the integral $(aa|ab)$, a π overlap-charge interacting with a π atomic charge. For a and b STO's, the integral has a value of 3.58 ev. For a and b LOAO's, the value is -0.09 ev.[22] The same integral calculated with Gram-Schmidt OAO's (GSOAO's) is about -1 ev. (For mathematical definitions, see Chapter III.)

The LOAO's provide maximum simplification of the math involved in doing an MO calculation.

Another advantage which LOAO's have over other OAO's is that they are symmetrically orthogonalized functions. For a simple homonuclear molecule, the electron densities of LOAO's coincide exactly with the densities predicted by Mulliken population analysis[43] of MO's expanded in an AO-set. Other OAO's (such as GSOAO's) are not symmetrical, and the atomic populations predicted by them are not symmetrical even for a simple homonuclear molecule such as H_2. For these OAO's, to get accurate charge densities one must transform the OAO coefficients to AO coefficients and do a population analysis, such as the Mulliken analysis.

For heteronuclear systems (unsymmetric systems), the LOAO's do not predict populations which agree with Mulliken population analysis. The difference is due to the fact that the LOAO's are multi-centered functions. If we wish to assign an electronic charge, calculated for a multi-centered function, to an atomic center, we can assign the charge only if the charge approximately coincides with that calculated for an AO.

The use of LOAO's involves the expansion $\bar{\Phi} = \Sigma_j C_j^{LOAO} \phi_j$ where $\bar{\Phi}$ is

a given molecular orbital, C_j^{LOAO} are the LOAO expanison coefficients for that MO, and ϕ_j are the LOAO's. The question naturally arises as to how well the molecular orbitals given by the LOAO expansion represent the electron distribution in a molecule.

The standard way to determine the electron distribution for molecules where expansion of the MO's has been carried out in an overlapping atomic orbital basis (AO's), $\bar{\Phi} = \Sigma_j C_j \Phi_j$, is that suggested by Mulliken and termed population analysis. For a simple diatomic molecule AB with AO's Φ_a and Φ_b the LOAO expansion coefficients are related to the AO expansion coefficients in following way:

$$C_a^{LOAO} = E\ C_a + (S/2E)\ C_b$$

and (12)

$$C_b^{LOAO} = (S/2E)\ C_a + E\ C_b,$$

where $E = \{[1 + (1 - S^2)^{\frac{1}{2}}]/2\}^{\frac{1}{2}}$, and S is the integral representing the overlap of Φ_a and Φ_b (see Chapter III). To obtain the electron density for the doubly occupied MO using the LOAO expansion each LOAO coefficient is squared and multiplied by a factor of two. This operation produces the following LOAO populations:

$$P_a^{LOAO} = 2\ [E^2 C_a^{\,2} + (S^2/4E^2)\ C_b^{\,2} + S\ C_a C_b]$$

and (13)

$$P_b^{LOAO} = 2\ [E^2 C_b^{\,2} + (S^2/4E^2)\ C_b^{\,2} + S\ C_a C_b].$$

The Mulliken population analysis method produces the following electronic populations:

$$P_a^{AO} = 2\ (C_a^{\,2} + S\ C_a C_b) \quad \text{and} \quad P_b^{AO} = 2\ (C_b^{\,2} + S\ C_a C_b). \qquad (14)$$

The Mulliken population analysis is identical to the LOAO population analysis if and only if $C_a = C_b$, that is if the molecule is homonuclear. If the molecule is heteronuclear then the accurate way to obtain a population analysis from the LOAO coefficients is to transform these coefficients to AO coefficients and perform a Mulliken population analysis. For a large molecule, however, this is impractical, and the LOAO populations must be assumed to adequately represent the electron distribution.

The LOAO populations have been computed using the previous equations for P_a^{LOAO} and P_b^{LOAO} and compared to the populations given by the more accurate Mulliken population analysis. This has been done for several sets of LOAO coefficients and for two different overlaps, S = 0.250 and S = 0.500. The results of these calculations and the errors in the LOAO populations when compared to the Mulliken populations are given in Table 1.

An overlap of 0.250 is representative of typical π-system overlaps, and an overlap of 0.500 is representative of some of the overlaps found in σ-systems. If we are to keep the error in the orbital populations for a given MO below about ten per cent, then we are restricted to LOAO coefficient ratios of say 2.5 or less for a typical π MO, but in σ-systems we are restricted to ratios of about 1.3 or less. This condition is often met by π MO's and less often met by σ MO's.

Although the results in Table 1 strongly imply that the MO by MO LOAO populations for σ MO's are unreliable, it is noted that the larger LOAO population is always less than the corresponding Mulliken AO population and that the smaller LOAO population is greater than its corresponding Mulliken population. For a many-MO molecule this indicates that a

Table 1

A Comparison of LOAO Populations and Mulliken AO Populations

C_a^{LOAO}/C_b^{LOAO}	P_a^{LOAO}	P_b^{LOAO}	P_a^{AO}	Percentage Error in P_a^{LOAO}	P_b^{AO}	Percentage Error in P_b^{LOAO}
S = 0.250						
1.1	1.096	0.904	1.098	-0.2	0.902	+0.2
1.3	1.256	0.744	1.265	-0.7	0.735	+1.2
1.5	1.384	0.616	1.397	-0.9	0.603	+2.2
2.0	1.600	0.400	1.620	-1.2	0.380	+5.3
3.0	1.800	0.200	1.826	-1.4	0.174	+15
4.0	1.8824	0.1176	1.9114	-1.5	0.0886	+33
5.0	1.9230	0.0770	1.9531	-1.5	0.0469	+64
S = 0.500						
1.1	1.096	0.904	1.110	-0.4	0.890	+1.6
1.3	1.256	0.744	1.296	-3.1	0.704	+5.7
1.5	1.384	0.616	1.444	-4.2	0.556	+11
2.0	1.600	0.400	1.693	-5.5	0.307	+23
3.0	1.800	0.200	1.9236	-6.4	0.0764	+160

summation of individual MO populations to produce a gross LOAO population will result in some cancellation of these errors. This cancellation may be expected to occur if the LOAO population overestimates the actual population in one MO and underestimates it in another.

Although a transformation of LOAO coefficients to AO coefficients and a Mulliken population analysis on the AO's could be carried out to achieve accurate MO electron distributions, the tremendous utility of the LOAO's is that reasonably accurate electron distributions can be obtained from the LOAO populations directly. The multi-centered nature of the LOAO's will, therefore, not interfere with our interpretation of the LOAO densities in terms of a single atomic center. This applies particularly to the π-electron MO theories.

CHAPTER III

THE MATHEMATICS OF ORTHOGONALIZATION OF ORBITALS

In order to develop an approximate MO theory which is both *ab initio* and neglects differential overlap, the first problem to solve is the problem of obtaining the LOAO's. Current methods of obtaining these functions by binomial expansions or by the numerical solution of the equation for a function of a symmetric matrix S,[33]

$$\underset{\sim}{U}^{+}\underset{\sim}{S}\,\underset{\sim}{U} = \underset{\sim}{D} \qquad (\underset{\sim}{D} \text{ diagonal})$$

then

$$f(\underset{\sim}{S}) = \underset{\sim}{U}\, f(\underset{\sim}{S})\, \underset{\sim}{U}^{+},$$

are unsatisfactory. The methods are time-consuming and do not provide uncomplicated expressions for the integrals necessary in a MO theory.

The search for a less complicated way to obtain closed-form LOAO's led first to the development of a transformation method of obtaining GSOAO's. This method allows one to write the GSOAO's directly in terms of the AO set rather than via the usual algorithm.[44] The desirability of this improvement was recognized by Löwdin who proposed a way of improving the Gram-Schmidt procedure different from the method outlined here. This search also led to the conclusion that LOAO's are obtainable analytically only for systems of AO's which have cyclic symmetry (a cyclic S-matrix). An approximate method of obtaining LOAO's, suitable for non-cyclic molecules but only applicable to π-electron systems, is therefore proposed.

(A) Orthogonalization of Orbitals by a Transformation Theory

The problem of how to obtain an orthogonal set of functions from a non-orthogonal set may be stated in matrix language as the problem of solving the equation

$$\underset{\sim}{X}'\underset{\sim}{S}\,\underset{\sim}{X} = \underset{\sim}{1}, \tag{15}$$

where $\underset{\sim}{1}$ is the unit matrix, $\underset{\sim}{S}$ is the overlap matrix for an ordered overlapping set of orbitals, $\underset{\sim}{X}$ is the transformation matrix and $\underset{\sim}{X}'$ is $\underset{\sim}{X}$ transposed. $\underset{\sim}{S}_{nxn}$, the nxn overlap matrix, may be looked upon as the result of the following matrix multiplication:

$$\underset{\sim}{S}_{nxn} = (\Phi_1\Phi_2\ldots\Phi_n)'(\Phi_1\Phi_2\ldots\Phi_n), \tag{16}$$

where $(\Phi_1\Phi_2\ldots\Phi_n)$ is the row matrix of overlapping orbitals. "Multiplication" of any two elements of the matrices is defined as taking the inner product $\int\Phi_i^*\Phi_j d\tau$ of the two elements. Accordingly, $\underset{\sim}{1}_{nxn}$ is the result of the matrix multiplication

$$\underset{\sim}{1}_{nxn} = (\phi_1\phi_2\ldots\phi_n)'(\phi_1\phi_2\ldots\phi_n), \tag{17}$$

where $(\phi_1\phi_2\ldots\phi_n)$ is the row matrix of the orthonormal orbitals. The matrices $\underset{\sim}{S}_{nxn}$ and $\underset{\sim}{1}_{nxn}$ are often called the metric matrices for the AO and the OAO sets respectively. Using these expressions for $\underset{\sim}{S}$ and $\underset{\sim}{1}$, one obtains a general expression for $\underset{\sim}{X}'\underset{\sim}{S}\,\underset{\sim}{X} = \underset{\sim}{1}$ as

$$\underset{\sim}{X}'(\Phi_1\Phi_2\ldots\Phi_n)'(\Phi_1\Phi_2\ldots\Phi_n)\,\underset{\sim}{X} = (\phi_1\phi_2\ldots\phi_n)'(\phi_1\phi_2\ldots\phi_n). \tag{18}$$

The solution to equation (18) is

$$(\Phi_1\Phi_2\ldots\Phi_n)\,\underset{\sim}{X} = (\phi_1\phi_2\ldots\phi_n), \tag{19}$$

i.e. that $\underset{\sim}{X}$ is the matrix which transforms the overlapping set into the orthonormal set.

We may now consider the problem of solving the equation $\underset{\sim}{X}'\underset{\sim}{S}\ \underset{\sim}{X} = \underset{\sim}{1}$ to obtain the transformation matrix $\underset{\sim}{X}$. Let

$$\underset{\sim}{1} = \underset{\sim}{P}'\underset{\sim}{P}, \tag{20}$$

thus defining $\underset{\sim}{P}$ as an orthogonal matrix, and let

$$\underset{\sim}{S} = \underset{\sim}{Q}'\underset{\sim}{Q}. \tag{21}$$

(Obviously a matrix $\underset{\sim}{A}$ can be written as a product of another matrix and its transpose only if the matrix $\underset{\sim}{A}$ is symmetric. $\underset{\sim}{S}$ is symmetric.) Then one may substitute these equations into $\underset{\sim}{X}'\underset{\sim}{S}\ \underset{\sim}{X} = \underset{\sim}{1}$ to obtain

$$\underset{\sim}{X}'\underset{\sim}{Q}'\underset{\sim}{Q}\ \underset{\sim}{X} = \underset{\sim}{P}'\underset{\sim}{P}, \tag{22}$$

or

$$\underset{\sim}{Q}\ \underset{\sim}{X} = \underset{\sim}{P}. \tag{23}$$

Solving this matrix equation for $\underset{\sim}{X}$, one obtains

$$\underset{\sim}{X} = \underset{\sim}{Q}^{-1}\ \underset{\sim}{P}. \tag{24}$$

It is necessary to find $\underset{\sim}{Q}^{-1}$ in order to obtain $\underset{\sim}{X}$. $\underset{\sim}{Q}^{-1}$ exists since $\underset{\sim}{Q}$ is non-singular. $\underset{\sim}{Q}^{-1}$ may be found by solving the matrix equation

$$\underset{\sim}{Q}'\underset{\sim}{Q} = \underset{\sim}{S} \tag{25}$$

for $\underset{\sim}{Q}$ and then finding $\underset{\sim}{Q}^{-1}$.

From Cullis[45], the solution of this type of equation has the general form

$$\underset{\sim}{Q} = \underset{\sim}{U}\ \underset{\sim}{P}_a, \tag{26}$$

where $\underset{\sim}{U}$ is a unitary matrix and $\underset{\sim}{P}_a$ is a particular solution of the equation. Since we are dealing here with real numbers, let $\underset{\sim}{U} = \underset{\sim}{O}$ where $\underset{\sim}{O}$ is an orthogonal matrix. Substituting this form for $\underset{\sim}{Q}$ into the equation $\underset{\sim}{X} = \underset{\sim}{Q}^{-1}\ \underset{\sim}{P}$, one obtains

$$\underset{\sim}{X} = (\underset{\sim}{O}\ \underset{\sim}{P}_a)^{-1}\ \underset{\sim}{P}, \tag{27}$$

which becomes

$$\underset{\sim}{X} = \underset{\sim}{P}_a^{-1} \underset{\sim}{Q}^{-1} \underset{\sim}{P}. \tag{28}$$

By definition $\underset{\sim}{Q}^{-1} = \underset{\sim}{Q}'$ and with this substitution we have

$$\underset{\sim}{X} = \underset{\sim}{P}_a^{-1} \underset{\sim}{Q}' \underset{\sim}{P}. \tag{29}$$

Since the product of two orthogonal matrices is orthogonal, one may set $\underset{\sim}{Q}' \underset{\sim}{P} = \underset{\sim}{B}$, $\underset{\sim}{B}$ being any orthogonal matrix. This results in the following form for $\underset{\sim}{X}$:

$$\underset{\sim}{X} = \underset{\sim}{P}_a^{-1} \underset{\sim}{B}. \tag{30}$$

$\underset{\sim}{X}$ may be found provided we specify the orthogonal matrix $\underset{\sim}{B}$ and provided we can find the inverse of a particular solution to the equation $\underset{\sim}{Q}' \underset{\sim}{Q} = \underset{\sim}{S}$.

One particular solution to such an equation may be obtained using the following relation[46]:

$$\lambda = (\Delta_k \, \Delta_{k+1})^{-\frac{1}{2}} \, [0, \, \ell]_1^{k, m-k}, \tag{31}$$

where

λ = the $\lambda^{\underline{\text{th}}}$ row of $\underset{\sim}{P}_a$,

$k = \lambda - 1$,

m = the total number of columns in $\underset{\sim}{P}_a$,

and Δ_k = the $k^{\underline{\text{th}}}$ diagonal minor determinant in the series of leading diagonal minor determinants. (For example, $\Delta_0 = 1$, and Δ_1 is the first element on the diagonal.) The notation $]_1^{k, m-k}$ indicates that there are k zeros and m-k entries of ℓ. The ℓ entries are always subscripted ℓ_{11}, ℓ_{12}, ℓ_{13}, ... regardless of which row of the matrix is being obtained. The first element is always ℓ_{11}. These entries $\ell_{\mu\nu}$ are obtained from the equation

$$\ell_{\mu\nu} = \begin{bmatrix} 1,2,\ldots,k,k+\nu \\ S \\ 1,2,\ldots,k,k+\mu \end{bmatrix}. \tag{32}$$

$\ell_{\mu\nu}$ is the determinant of (S_{ij}), where $i = 1,2,\ldots,k,k+\mu$ and $j = 1,2,\ldots,k,k+\nu$. This method of solving for $\underset{\sim}{P}_a$ produces a matrix which is upper triangular. This makes it relatively easy to obtain the inverse $\underset{\sim}{P}_a^{-1}$.

For $\underset{\sim}{S}_{2x2}$, $\underset{\sim}{S}$ takes the following form:

$$\underset{\sim}{S} = \begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix}, \tag{33}$$

provided the AO's are normalized. Using the previously outlined procedure to find the orthogonal set of orbitals from the overlapping set, we need to find $\underset{\sim}{P}_a^{-1}$ for this 2x2 example. One obtains $\underset{\sim}{P}_a$, row by row, as

$$\text{Row 1} = (1, S)$$

and

$$\text{Row 2} = (1-S^2)^{-\frac{1}{2}} (0, 1-S^2),$$

or

$$\text{Row 2} = (0,(1-S^2)^{\frac{1}{2}}).$$

Putting together the rows we obtain the 2x2 matrix

$$\underset{\sim}{P}_a = \begin{bmatrix} 1 & S \\ 0 & (1-S^2)^{\frac{1}{2}} \end{bmatrix}. \tag{34}$$

To find the transformation matrix $\underset{\sim}{X}$ we employ the equation $\underset{\sim}{X} = \underset{\sim}{P}_a^{-1} \underset{\sim}{B}$ and select $\underset{\sim}{B}_{2x2} = \underset{\sim}{1}_{2x2}$. The result is

$$\underset{\sim}{X} = \begin{bmatrix} 1 & -S(1-S^2)^{-\frac{1}{2}} \\ 0 & (1-S^2)^{-\frac{1}{2}} \end{bmatrix} \tag{35}$$

The orthonormal set of functions generated by this transformation is simply

$$\phi_1' = \phi_1$$
$$\phi_2' = (1-S^2)^{-\frac{1}{2}} (\phi_2 - S\phi_1). \tag{36}$$

These functions are recognizable as the results of the familiar Gram-Schmidt orthogonalization process.[44]

To produce LOAO's we can retain the form generated for $\underset{\sim}{P}_a^{-1}$ and use a different $\underset{\sim}{B}$. In order to fix all the elements of $\underset{\sim}{B}$ we need to employ the well-known orthogonality conditions on the elements of $\underset{\sim}{B}$ plus one further condition on the elements. This condition is provided by the symmetric nature of the Löwdin orthogonalization. LOAO's in the 2x2 case have the following form:

$$\phi_1 = A\phi_1 + B\phi_2$$

and (37)

$$\phi_2 = B\phi_1 + A\phi_2.$$

For the LOAO ϕ_1 the coefficient of ϕ_1 is equal to the coefficient of ϕ_2 in the LOAO ϕ_2. The LOAO's in the general 2x2 case have a mirror-image symmetry. We return to the equation $\underset{\sim}{X} = \underset{\sim}{P}_a^{-1} \underset{\sim}{B}$, use the same $\underset{\sim}{P}_a^{-1}$ as was used in generating GSOAO's, but leave $\underset{\sim}{B}$ undetermined. This gives

$$\underset{\sim}{X} = \begin{bmatrix} 1 & -S(1-S^2)^{-\frac{1}{2}} \\ 0 & (1-S^2)^{-\frac{1}{2}} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix}. \tag{38}$$

Doing the matrix multiplication, employing the transformation relationship $\phi = \Phi\underset{\sim}{X}$ and using all the conditions placed upon the elements of $\underset{\sim}{B}$, one can solve for these elements. One obtains

$$\underset{\sim}{B} = \begin{bmatrix} E & S/2E \\ -S/2E & E \end{bmatrix}, \tag{39}$$

where

$$E = \{[1 + (1-S^2)^{\frac{1}{2}}] / 2\}^{\frac{1}{2}}.$$

This expression for $\underset{\sim}{B}$, when substituted into the relation $\underset{\sim}{X} = \underset{\sim}{P}_a^{-1} \underset{\sim}{B}$, produces

$$\underset{\sim}{X} = (1-S^2)^{-\frac{1}{2}} \begin{bmatrix} E & -S/2E \\ -S/2E & E \end{bmatrix}, \tag{40}$$

and the transformation to obtain ϕ gives

$$\phi_1 = (1-S^2)^{-\frac{1}{2}} (E\phi_1 - (S/2E)\phi_2)$$

and (41)

$$\phi_2 = (1-S^2)^{-\frac{1}{2}} (E\phi_2 - (S/2E)\phi_1).$$

These are the LOAO's in the 2x2 case. A different representation for these 2x2 solutions has been obtained by Parr.[22]

This result for the general 2x2 case implies that closed-form expressions for ϕ can be obtained only when the LOAO's have the mirror-image symmetry. It appears that it is only under this circumstance that a unique solution for the matrix $\underset{\sim}{B}$ can be obtained from the procedure outlined in the 2x2 example. This requirement seems to be the same as requiring that the overlap matrix be cyclic[30] and would suggest that the only closed-form expressions for LOAO's are those for $\underset{\sim}{S}$ a cyclic matrix. One can then conclude that no general closed-form expressions for LOAO's applicable to molecules with non-cyclic $\underset{\sim}{S}$ matrices can be obtained.

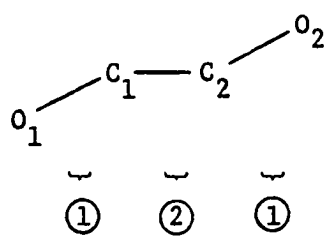
(B) Approximate LOAO's for π-Electron Systems

One can generate approximate LOAO's from π AO's by orthogonalizing the π AO's pairwise. In σ-systems, where for a pair of atoms there is

more than one pair of overlapping AO's, the technique outlined here is probably not applicable. To employ the technique one orthogonalizes a pair of AO's using the 2x2 transformation of the previous section to produce LOAO's. These LOAO's are then orthogonalized to any other AO's in the system which overlap appreciably with them.

Since there is little mathematical formalism associated with this procedure, it is best to illustrate it with a specific example. A reasonably general example is the π-electron part of the glyoxal molecule. It is felt that glyoxal represents, as far as this procedure is concerned, a general example of a π-electron system. If this orthogonalization procedure produces acceptable results for glyoxal, it is not difficult to accept that it will produce acceptable results for butadiene, hexatriene, pyridine, anthracene, etc. The AO's chosen for glyoxal are STO's with orbital exponents of 1.60 for carbon p_π and 2.20 for oxygen p_π. These orbital exponents were determined variationally for the CO molecule.[47] The bond lengths and bond angles are those of Lu Valle and Schomaker.[48]

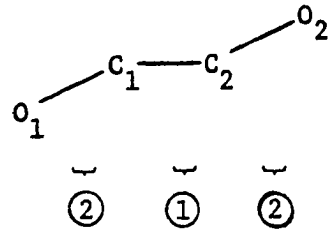
There are two possible ways of orthogonalizing the π AO's of glyoxal pairwise. The first is termed Option A.



Option A

In Option A the π AO's on O_1 and C_1 are orthogonalized using the 2x2 transformation matrix and the π AO's on C_2 and O_2 are orthogonalized in the same way. These two steps produce the LOAO's ϕ_{O_1}, ϕ_{C_1}, ϕ_{C_2}, and

ϕ_{O_2}. The LOAO's ϕ_{C_1} and ϕ_{C_2} are then orthogonalized in 2x2 fashion to produce a new pair of LOAO's. Option A therefore results in the set of approximate LOAO's ϕ_{O_1}, ϕ_{C_1}', ϕ_{C_2}', and ϕ_{O_2}. Since the overlap of the AO pair O_1-C_2 and the overlap of the AO pair O_1-O_2 are both small to begin with, it is not necessary to further complicate the picture by orthogonalizing these pairs. The second option is termed Option B.



Option B

In Option B the AO's on C_1 and C_2 are first orthogonalized pairwise to produce the LOAO's ϕ_{C_1} and ϕ_{C_2}. Next ϕ_{C_1} is orthogonalized to the AO on O_1, and ϕ_{C_1} is orthogonalized to the AO on O_2. This produces a LOAO set for Option B of ϕ_{O_1}, ϕ_{O_2}, ϕ_{C_1}', and ϕ_{C_2}'.

In order to establish that the technique exhibited for glyoxal's π AO's produces good approximations to LOAO's it is necessary to show that (1) the functions produced by Options A and B are approximately orthonormal and (2) that these approximately orthonormal functions have the LOAO property of being symmetrically orthogonal. The first requirement may be checked by comparing the overlap matrix for the original π AO's to the overlap matrices for the approximate LOAO's. To meet the second requirement it must be shown that regardless of whether Option A or Option B is employed to produce the approximate LOAO's the resulting functions are very similar. Only for LOAO's should this be the case. If one uses a non-symmetrical orthogonalization procedure, such as the Gram-Schmidt orthogonalization

method, the functions produced by pairwise orthogonalization would vary greatly depending upon the order in which the pairs were orthogonalized. Since the approximate LOAO's are developed here with an eye towards application to π-electron MO theory, to show that the functions of Options A and B are roughly similar it should suffice to show that the corresponding one-electron matrix elements computed with both Options A and B are roughly equal. If these matrix elements are equal then a π-MO calculation using either set of approximate LOAO's will produce LOAO coefficients which are equal. Wave functions for both Options A and B would then have the same physical significance.

The overlap matrix for the AO's is shown in Table 2. These overlaps were determined using the overlap tables of Mulliken, Rieke, Orloff, and Orloff.[49] The overlaps in Table 2 were used to compute the approximate LOAO's of Options A and B. Each option gives the LOAO's as expansions in AO's. The coefficients C_{ij} for the expansion $\phi_j = \Sigma_i C_{ij} \phi_i$ are listed in Table 3. Inspection of the coefficients in Table 3 indicates that the functions produced by Option A and Option B are very similar.

The overlap matrices for the approximate LOAO's were computed using the functions listed in Table 3 and the overlaps of Table 2. The overlap matrix for the functions of Option A is presented in Table 4, and the overlap matrix for Option B is in Table 5. Both options have overlap matrices which are to an excellent approximation simply the unit matrix. Mathematically this can be stated $(\phi_{O_1} \quad \phi_{C_1}' \quad \phi_{C_2}' \quad \phi_{O_2})'(\phi_{O_1} \quad \phi_{C_1}' \quad \phi_{C_2}' \quad \phi_{O_2}) \cong \underset{\sim}{1}$. The requirement that the approximate LOAO's are approximately orthonormal is therefore met by the functions of both Options A and B.

The one-electron matrix elements which we shall compare here for

Table 2

Overlap Matrix for AO's

	Φ_{O_1}	Φ_{C_1}	Φ_{C_2}	Φ_{O_2}
Φ_{O_1}	1.00	0.238	0.023	0.000
Φ_{C_1}	0.238	1.00	0.221	0.023
Φ_{C_2}	0.023	0.221	1.00	0.238
Φ_{O_2}	0.000	0.023	0.238	1.00

Table 3

Coefficients in the Expansion of LOAO's

in AO's ($\phi_j = \Sigma_i C_{ij} \Phi_i$)

j	$C_{O_1 j}$	$C_{C_1 j}$	$C_{C_2 j}$	$C_{O_2 j}$
		Option A		
O_1	1.022	-0.1233	0.00	0.00
C_1	-0.1258	1.042	-0.1188	0.0143
		Option B		
O_1	1.023	-0.1270	0.0142	0.00
C_1	-0.1250	1.042	-0.1170	0.00

Table 4

Overlap Matrix for Option A

	ϕ_{O_1}	$\phi_{C_1'}$	$\phi_{C_2'}$	ϕ_{O_2}
ϕ_{O_1}	1.000	0.000	-0.003	0.000
$\phi_{C_1'}$	0.000	1.001	-0.002	-0.003
$\phi_{C_2'}$	-0.003	-0.002	1.001	0.000
ϕ_{O_2}	0.000	-0.003	0.000	1.000

Table 5

Overlap Matrix for Option B

	ϕ_{O_1}	ϕ_{C_1}'	ϕ_{C_2}'	ϕ_{O_2}
ϕ_{O_1}	1.001	0.000	-0.007	0.000
ϕ_{C_1}'	0.000	1.001	-0.001	-0.007
ϕ_{C_2}'	-0.007	-0.001	1.001	0.000
ϕ_{O_2}	0.000	-0.007	0.000	1.001

glyoxal are of the following form:

$$\alpha_j = (\phi_j(1) \mid H(1) \mid \phi_j(1)) \tag{42}$$

and

$$\beta_{ij} = (\phi_i(1) \mid H(1) \mid \phi_j(1)). \tag{43}$$

The one-electron Hamiltonian operator is taken as a sum of the kinetic energy operator and the nuclear framework potential seen by an electron. The potential due to the core of σ-electrons is not included in this calculation. It is not necessary to include this potential in order to prove that the second requirement on the approximate LOAO's is fulfilled. All energy integrals needed in these calculations were obtained using Roothaan's formulas,[50] with the exception of the three-center nuclear attraction integrals. The three-center integrals were obtained using the well-known Mulliken approximation.[24]

The results of these calculations are shown in Table 6. The differences between the α's calculated by Options A and B are only on the order of two-tenths of an electron volt. This would represent a small error in a π-electron MO calculation, and for all practical purposes Options A and B produce the same values for α. The differences in the β's for Options A and B are again on the order of two-tenths of an electron volt. The β's calculated using the Option A LOAO's and the Option B LOAO's are effectively equal. These results strongly indicate that the approximate LOAO's are not only orthonormal but have the important symmetry property of exact LOAO's. Since the approximate LOAO's have this property, the pairwise orthogonalization method can be initiated with any pair in the molecule.

The β's calculated for glyoxal may be compared to the β's used in

Table 6

One-Electron Matrix Elements for Options A and B Orbitals (units are au except where otherwise indicated)

$\underline{\alpha}$

	Carbon	Oxygen
Option A	-10.345	-11.441
Option B	-10.338	-11.447
Difference (A-B)	- 0.008	+ 0.006
Difference (ev)	- 0.21	+ 0.16

$\underline{\beta}$

	$\beta_{O_1C_1}$	$\beta_{C_1C_2}$
Option A	- 0.102	- 0.064
Option B	- 0.095	- 0.058
Difference (A-B)	- 0.007	- 0.006
Difference (ev)	- 0.18	- 0.16

semi-empirical MO theories. Sidman[51] has done π-electron calculations on molecules containing the carbonyl group, including glyoxal, using Pariser-Parr-Pople theory. For these calculations he used β_{OC} = -3.00 ev and β_{CC} = -1.68 ev. The much more recent CNDO method as used by Jaffé and Del Bene[11] to predict electronic spectra of molecules obtains β for π AO's from the equation $\beta^{\pi}_{\mu\nu} = \frac{1}{2}(0.585)(\beta^{\circ}_{A} + \beta^{\circ}_{B}) S_{\mu\nu}$. With β°_{C} of -17 ev, β°_{O} of -45 ev,[12] and with overlaps $S_{\mu\nu}$ for STO's with orbital exponents 1.625 for carbon and 2.275 for oxygen, β_{CO} = -4.04 ev and β_{CC} = -2.12 ev. Option A orbitals give β_{CO} = -2.77 ev and β_{CC} = -1.74 ev. Option B orbitals give β_{CO} = -2.58 ev and β_{CC} = -1.58 ev. The β's calculated with approximate LOAO's agree more closely with the β's of the older Pariser-Parr-Pople method than with the β's of the newer CNDO method.

(C) Summary

In this chapter, the Löwdin orthogonalized orbitals have been derived through a matrix formalism. The results of this derivation suggest that LOAO's are not generally derivable in a convenient closed-form except in the special circumstance that the S-matrix is cyclic. The formal results for the case of a simple 2x2 S-matrix are, however, useful as a basis for obtaining approximate LOAO's for π-systems.

The approximate LOAO's generated by pairwise orthogonalization are acceptably orthonormal and do have the LOAO property of symmetry. The approximate method outlined here probably works as well as it does due to the fact that the only AO overlaps in the glyoxal example which are appreciable are the nearest-neighbor overlaps. The non-nearest-neighbor AO overlaps are small to begin with and are reduced to less than one-third their original magnitude by the orthogonalization process. These features

of the AO S-matrix can be expected to occur generally in π-systems. The LOAO property of symmetry allows one the very important freedom of beginning pairwise orthogonalization with any pair in the molecule.

The β's computed for the π orbitals of glyoxal compare favorably with the β's obtained in semi-empirical MO theories. This suggests that these functions would make a useful basis for generating equations for α's and β's in an *ab initio* no-overlap π-electron theory.

CHAPTER IV

THE DERIVATION OF AN APPROXIMATE SCF THEORY FOR π-ELECTRON SYSTEMS

In this chapter, the Roothaan equations for the MO expansion coefficients of a set of AO's are rewritten so that they are suitable for (1) LOAO's and (2) π-electron systems. Through a systematic set of approximations, beginning with the approximate LOAO's developed in the previous chapter, these equations will be developed into a less formidable approximate *ab initio* π-electron MO theory. The approximations developed in order to simplify the calculations are checked against more accurate calculations where possible.

(A) The Roothaan Equations for No-Overlap π-Electron Molecular Orbital Theory

The familiar Roothaan equations[52] have, when written in an overlapping atomic orbital (AO) basis set, the following form:

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \sum_{\nu} S_{\mu\nu} C_{\nu i} \varepsilon_i .$$

$F_{\mu\nu}$ may be defined by the equation

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu},$$

where

$$H_{\mu\nu} = \int \bar{\Phi}_{\mu} \left[-\frac{1}{2} \nabla^2 - \sum_{A} V_A(r) \right] \Phi_{\nu} d\tau$$

and

$$G_{\mu\nu} = \sum_{\lambda,\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\nu\lambda)\right].$$

$P_{\lambda\sigma}$ is defined by the equation

$$P_{\lambda\sigma} = 2 \sum_{i}^{\substack{occ. \\ MO's}} \bar{C}_{i\lambda} C_{i\sigma},$$

and the overlap $S_{\mu\nu}$ is defined by

$$S_{\mu\nu} = \int \bar{\Phi}_{\mu} \Phi_{\nu} d\tau.$$

$H_{\mu\nu}$ is the AO matrix element over the sum of the kinetic energy and nucleus-electron-attraction potential operators. $G_{\mu\nu}$ is the AO matrix element of the Hartree-Fock electron-repulsion operator, written in the AO basis. The $P_{\lambda\sigma}$ are elements of the bond order matrix, the $(\mu\nu|\lambda\sigma)$ are electron-repulsion integrals, and the ε_i are the orbital energies.

If the basis set of atomic orbitals is an orthogonal set, specifically LOAO's, then the Roothaan equations for this set are

$$\sum_{\nu} F_{\mu\nu}^{LOAO} C_{\nu i}^{LOAO} = C_{\mu i}^{LOAO} \varepsilon_i. \tag{44}$$

$F_{\mu\nu}^{LOAO}$ is defined as

$$F_{\mu\nu}^{LOAO} = H_{\mu\nu}^{LOAO} + G_{\mu\nu}^{LOAO},$$

where

$$H_{\mu\nu}^{LOAO} = \int \bar{\phi}_{\mu} \left[-\frac{1}{2}\nabla^2 - \sum_{A} V_A(r)\right] \phi_{\nu} d\tau$$

and

$$G_{\mu\nu}^{LOAO} = \sum_{\lambda,\sigma} P_{\lambda\sigma}^{LOAO} \left[(\phi_\mu\phi_\nu|\phi_\lambda\phi_\sigma) - \frac{1}{2}(\phi_\mu\phi_\sigma|\phi_\nu\phi_\lambda)\right].$$

Here the LOAO's are indicated by ϕ rather than the AO notations of Φ or simply the subscript. The LOAO bond-order matrix $P^{LOAO}_{\lambda\sigma}$ is defined by

$$P^{LOAO}_{\lambda\sigma} = 2 \sum_{i}^{\substack{occ. \\ MO's}} \bar{C}^{LOAO}_{i\lambda} C^{LOAO}_{i\sigma},$$

and the elements of the overlap matrix are simply $S_{\mu\nu} = \delta_{\mu\nu}$ (δ = the Kronecker delta). The matrix $\underset{\sim}{S}$ is therefore the unit matrix $\underset{\sim}{1}$.

The performing of the SCF iteration procedure to find the MO's in terms of the LOAO's requires that we be able to determine the matrix elements $F^{LOAO}_{\mu\nu}$. Since this work is restricted to π-electron MO theory it is helpful to write these matrix elements so that they look like the sum of a π-core interaction and a π-π interaction. This is done subject to the conditions of σ-π separability outlined by Parr.* These conditions define what we mean by a π MO and what we mean by a σ MO. Writing $F^{LOAO}_{\mu\nu}$ in this fashion, we obtain

$$F^{LOAO}_{\mu\nu} = (\phi_\mu(1)|-\tfrac{1}{2}\nabla^2_1 - \sum_A V_A(1) + \sum_{\lambda,\sigma'}^{\substack{occ.\ \sigma \\ MO's}} P^{LOAO}_{\lambda\sigma'} \{\phi_\lambda(2)\phi_{\sigma'}(2)$$

$$- \tfrac{1}{2}\phi_\lambda(2)\,\tilde{P}_{1,2}\,\phi_{\sigma'}(2)\}|\phi_\nu(1)) + \sum_{\lambda,\sigma}^{\substack{occ.\ \pi \\ MO's}} P^{LOAO}_{\lambda\sigma}\,[(\phi_\mu\phi_\nu|\phi_\lambda\phi_\sigma) - \tfrac{1}{2}(\phi_\mu\phi_\sigma|\phi_\nu\phi_\lambda)].$$

$F^{LOAO}_{\mu\nu}$ is, from this point on, intended to apply to π-electrons only, i.e. ϕ_μ and ϕ_ν are π LOAO's. The electronic coordinates 1 and 2 are included for clarity in the first term of this expression (the π-core term). The coordinates are understood in the second term (the π-π interaction term).

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* See reference 22, page 42.

$\tilde{P}_{1,2}$ is the operator which permutes coordinates 1 and 2.

The first simplification which will be made in $F_{\mu\nu}^{LOAO}$ is to call the operator

$$-\frac{1}{2}\nabla_1^2 - \sum_A V_A(1) + \sum_{\lambda,\sigma'}^{\substack{occ.\ \sigma \\ MO's}} P_{\lambda\sigma'}^{LOAO} \{\phi_\lambda(2)\phi_{\sigma'}(2) - \frac{1}{2}\phi_\lambda(2)\,\tilde{P}_{1,2}\,\phi_{\sigma'}(2)\}$$

the operator V_{core}. V_{core} is the operator which includes the kinetic energy and the π-core potential. To simplify the expression for $F_{\mu\nu}^{LOAO}$ still further, we must introduce our first approximation. The π-π interaction part of $F_{\mu\nu}^{LOAO}$ may be simplified by requiring that all π-repulsion integrals which involve the charge densities of overlapping LOAO's be zero and that all other π-repulsion integrals have the same value that they would have if computed with corresponding AO's. This, formally the well-known ZDO approximation, has been shown to be valid for a LOAO basis set by Parr.[22] Application of these simplifications results in the following approximate form for $F_{\mu\nu}^{LOAO}$:

$$F_{\mu\mu}^{LOAO} = (\phi_\mu(1)|V_{core}|\phi_\mu(1)) + \sum_{\sigma}^{\substack{occ.\ \pi \\ MO's}} P_{\sigma\sigma}^{LOAO}\,(\mu\mu|\sigma\sigma) - \frac{1}{2}P_{\mu\mu}^{LOAO}\,(\mu\mu|\mu\mu) \quad (45)$$

and

$$F_{\mu\nu}^{LOAO} = (\phi_\mu(1)|V_{core}|\phi_\nu(1)) - \frac{1}{2}P_{\mu\nu}^{LOAO}\,(\mu\mu|\nu\nu),\ \text{if}\ \mu \neq \nu. \quad (46)$$

Set

$$\alpha_\mu^{LOAO} = (\phi_\mu(1)|V_{core}|\phi_\mu(1)), \quad (47)$$

and

$$\beta_{\mu\nu}^{LOAO} = (\phi_\mu(1)|V_{core}|\phi_\nu(1)). \quad (48)$$

With these substitutions, we have

$$F_{\mu\mu}^{LOAO} = \alpha_{\mu}^{LOAO} + \sum_{\sigma}^{\substack{occ.\ \pi \\ MO's}} P_{\sigma\sigma}^{LOAO} (\mu\mu|\sigma\sigma) - \frac{1}{2} P_{\mu\mu}^{LOAO} (\mu\mu|\mu\mu) \tag{49}$$

and

$$F_{\mu\nu}^{LOAO} = \beta_{\mu\nu}^{LOAO} - \frac{1}{2} P_{\mu\nu}^{LOAO} (\mu\mu|\nu\nu). \tag{50}$$

(B) Derivation of $\beta_{\mu\nu}^{LOAO}$ and α_{μ}^{LOAO}

Specification of the LOAO's in terms of AO's is required in order to derive the α_{μ}^{LOAO} and $\beta_{\mu\nu}^{LOAO}$ terms in equations (49) and (50). Since general expressions for exact LOAO's are mathematically cumbersome, we shall use instead approximate LOAO's, produced by the pairwise orthogonalization process. In this scheme, the LOAO's obtained from a pair of AO's are exact. Approximate LOAO's are obtained from a set of three or more AO's, where each AO is on a different atomic center, by orthogonalizing a pair of AO's to produce a pair of LOAO's. These LOAO's are then orthogonalized pairwise to any other AO's which overlap appreciably with them. (See Chapter III.)

To derive α_{μ}^{LOAO} and $\beta_{\mu\nu}^{LOAO}$, four different geometries will be assumed for the atomic centers. The four geometries are shown in figure 1. These should account for the possible geometries taken by the atoms of a π-electron system. Comparison of the specific equations for $\beta_{\mu\nu}^{LOAO}$ derived for each case should produce a general equation. A general equation for α_{μ}^{LOAO} can be derived using the same technique.

(1) Derivation of $\beta_{\mu\nu}^{LOAO}$

Case A is a two-AO case. The exact LOAO's are as follows:

$$\phi_x = (1 - S_{xy}^2)^{-\frac{1}{2}} \{Ex - (S/2E)y\}$$

and

$$\phi_y = (1 - S_{xy}^2)^{-\frac{1}{2}} \{Ey - (S/2E)x\},$$

where

$$E = [\{1 + (1 - S_{xy}^2)^{\frac{1}{2}}\} / 2]^{\frac{1}{2}}.$$

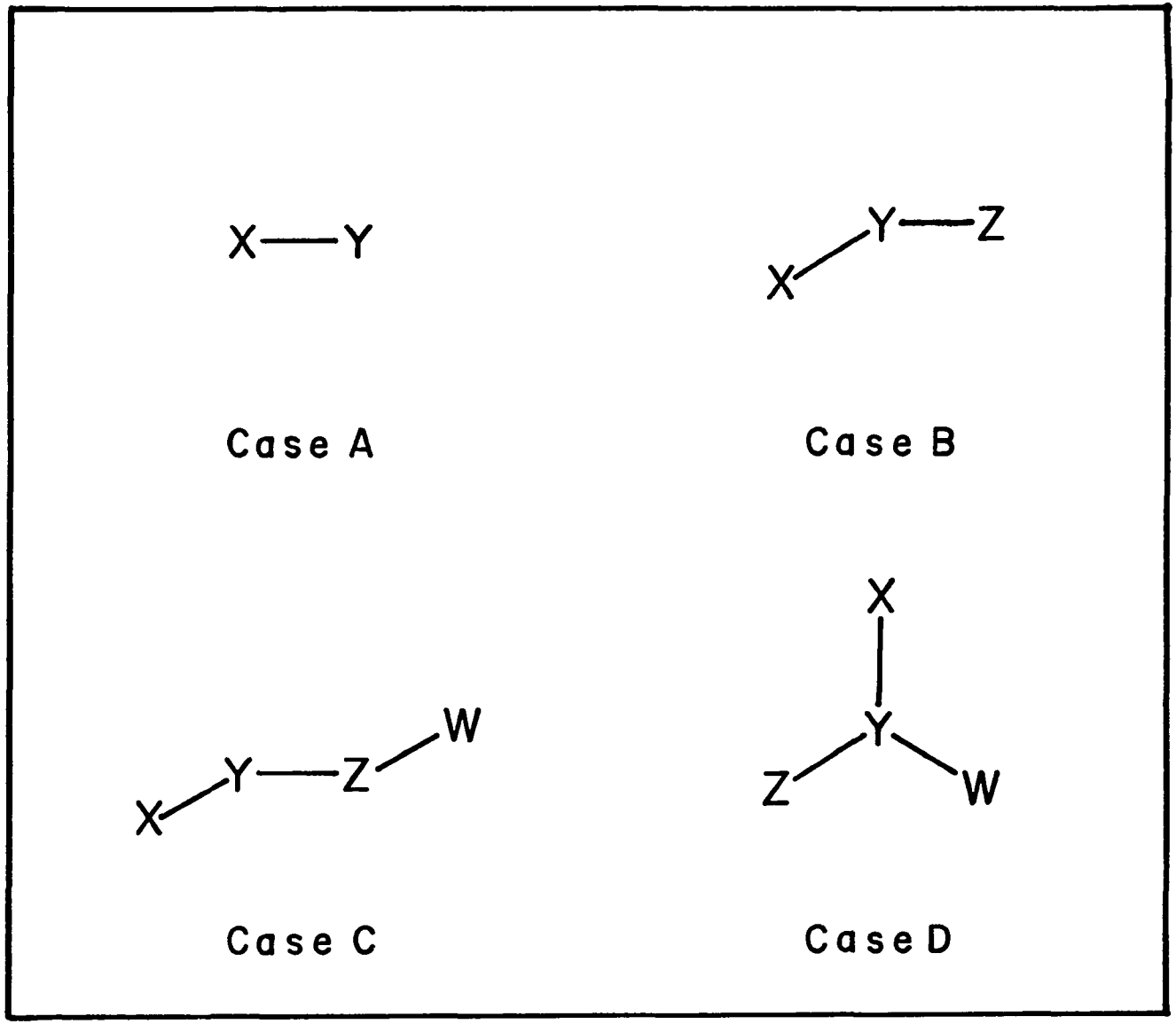


Figure 1

Specific geometries considered in the derivations.

Substituting these LOAO's into equation (48), one obtains

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-1} [(x|V_{core}|y) - (S_{xy}/2) \{(x|V_{core}|x) + (y|V_{core}|y)\}]. \quad (51)$$

This equation gives β_{xy}^{LOAO} in terms of the AO's x and y. If one recalls that the Mulliken approximation for an AO density function xy is $xy = \frac{1}{2} S_{xy}(xx + yy)$, then it is apparent that the term in square brackets is the error in the Mulliken approximation for the density xy. Equation (51) may then be written

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-1} \quad [\text{Error in the Mulliken approximation}],$$

or

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-1} (EM)_{x,y}. \quad (52)$$

Case B is a three-AO case. Approximate LOAO's may be derived for this case by orthogonalizing the AO's Φ_x and Φ_y to give a LOAO pair ϕ_x and ϕ_y. ϕ_y is then orthogonalized to the AO Φ_z to give ϕ_y' and ϕ_z. The AO's Φ_x and Φ_z are assumed to have negligible overlap. The LOAO's, so derived, have the following form:

$$\phi_x = (1 - S_{xy}^2)^{-\frac{1}{2}} \{E_{xy}\, x - (S_{xy}/2E_{xy})y\},$$

$$\phi_y' = (1 - S_{y'z}^2)^{-\frac{1}{2}} \{E_{y'z}\, \phi_y - (S_{y'z}/2E_{y'z})z\},$$

and

$$\phi_z = (1 - S_{y'z}^2)^{-\frac{1}{2}} \{E_{y'z}\, z - (S_{y'z}/2E_{y'z})\phi_y\}.$$

In these expressions, we define

$$E_{ij} = [\{1 + (1 - S_{ij}^2)^{\frac{1}{2}}\} / 2]^{\frac{1}{2}},$$

where i and j are AO's, except if primed. If one of the subscripts is

primed, it refers to a previously obtained LOAO. The same convention applies to S_{ij}. In this example, the equation for ϕ_y should be obvious from consideration of Case A.

To derive β_{xy}^{LOAO} for the three-center case, we need to substitute ϕ_x and ϕ_y' into equation (48). When this has been done, and some algebraic simplification on the resulting expression carried out, we obtain

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{y',z}^2)^{-\frac{1}{2}} [(1 - S_{xy}^2)^{-\frac{1}{2}} E_{y',z} \{(x|V_{core}|y) - \frac{1}{2} S_{xy}((x|V_{core}|x) + (y|V_{core}|y))\} - (S_{y',z}/2E_{y',z}) \{E_{xy}(x|V_{core}|z) - (S_{xy}/2E_{xy}) (y|V_{core}|z)\}]. \quad (53)$$

The term $\{(x|V_{core}|y) - \frac{1}{2} S_{xy}((x|V_{core}|x) + (y|V_{core}|y))\}$ is just $(EM)_{x,y}$. Substituting this into equation (53), we have

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{y',z}^2)^{-\frac{1}{2}} [(1 - S_{xy}^2)^{-\frac{1}{2}} E_{y',z}(EM)_{x,y} - (S_{y',z}/2E_{y',z}) \{E_{xy}(x|V_{core}|z) - (S_{xy}/2E_{xy}) (y|V_{core}|z)\}]. \quad (54)$$

$S_{y',z}$ may be obtained from the definition of the overlap, $S_{y',z} = (\phi_y|z)$, and is

$$S_{y',z} = (1 - S_{xy}^2)^{-\frac{1}{2}} (\{E_{xy}\, y - (S_{xy}/2E_{xy})x\} \mid z).$$

Using properties of the inner-product, we obtain

$$S_{y',z} = (1 - S_{xy}^2)^{-\frac{1}{2}} \{E_{xy}\, S_{yz} - S_{xy}\, S_{xz}/2E_{xy}\}.$$

The first approximation introduced in deriving β_{xy}^{LOAO} is to set $S_{xz} = 0$. For π-systems, overlaps between next-nearest neighbors are roughly an order of magnitude less than overlaps between nearest neighbors. With

this approximation, we have

$$S_{y'z} \approx (1 - S_{xy}^2)^{-\frac{1}{2}} E_{xy} S_{yz}.$$

An even more approximate form for $S_{y'z}$ may be obtained by noting that, for π-orbital overlaps, $(1 - S_{xy}^2)^{-\frac{1}{2}} E_{xy}$ is roughly equal to unity. This allows one to crudely approximate $S_{y'z}$ by the overlap between corresponding AO's S_{yz}. The second approximation for $S_{y'z}$ is used to simplify the terms $E_{y'z}$ and $(1 - S_{y'z}^2)^{\frac{1}{2}}$. Using this approximation, we have

$$E_{y'z} \approx E_{yz}$$

and

$$(1 - S_{y'z}^2)^{\frac{1}{2}} \approx (1 - S_{yz}^2)^{\frac{1}{2}}.$$

The crude approximation of $S_{y'z}$ by S_{yz} causes little error. In each case, the overlap-squared is compared to unity, and the two terms are therefore not very sensitive to errors in the overlap. Where $S_{y'z}$ stands alone, it will be approximated using the first, and more accurate, relationship. These approximations are introduced into equation (54) to give

$$\begin{aligned}\beta_{xy}^{LOAO} = {} & (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{yz}^2)^{-\frac{1}{2}} [(1 - S_{xy}^2)^{-\frac{1}{2}} E_{yz}(EM)_{x,y} \\ & - \{((1 - S_{xy}^2)^{-\frac{1}{2}} E_{xy} S_{yz})/2E_{yz}\} \{E_{xy}(x|V_{core}|z) \\ & - (S_{xy}/2E_{xy}) (y|V_{core}|z)\}]. \end{aligned} \tag{55}$$

It is a consistent approximation that $(x|V_{core}|z)$, like S_{xz}, is equal to zero. When this approximation is made in equation (55), one obtains

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{yz}^2)^{-\frac{1}{2}} [(1 - S_{xy}^2)^{-\frac{1}{2}} E_{yz}(EM)_{x,y}$$

$$+ \{(1 - S_{xy}^2)^{-\frac{1}{2}} S_{yz} S_{xy}/4E_{yz}\} (y|V_{core}|z)]. \qquad (56)$$

The factor which is multiplied times $(y|V_{core}|z)$ is on the order of S^2. For π overlaps, S^2 is a small term. A crude approximation of the factor multiplied times such a small term should still give reasonable accuracy for β_{xy}^{LOAO}. We therefore approximate E_{yz} by taking $E_{yz} = 1$, and we approximate $(y|V_{core}|z)$ by setting it equal to -1.00 au. When these approximations are introduced in equation (56), β_{xy}^{LOAO} becomes*

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-1} (1 - S_{yz}^2)^{-\frac{1}{2}} [E_{yz}(EM)_{x,y} - S_{yz} S_{xy}/4]. \qquad (57)$$

This result allows β_{xy}^{LOAO} to be calculated from a knowledge of the AO-overlap matrix and a knowledge of the term $(EM)_{x,y}$.

There are two approximations leading to equation (57) which need special justification. The first is the approximation that $(y|V_{core}|z) = -1.00$ au. The second is that $(x|V_{core}|z) = 0$.

$(y|V_{core}|z)$ is a resonance integral for nearest-neighbor AO's. To show that this integral is about -1.00 au., we calculated it for the molecules H_2, HeH^+, and glyoxal. For H_2, at its equilibrium internuclear separation, we obtained $(1s_{H_1}|V_{core}|1s_{H_2}) = -0.961$ au. This calculation was performed using AO-integrals from Slater.[53] For HeH^+, at its equilibrium internuclear distance, with AO's whose exponents were determined

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* β_{yz}^{LOAO} may be calculated to good accuracy with an equation analagous to this equation. Although such an equation does not spring directly from the basis of LOAO's used to calculate β_{xy}^{LOAO}, calculations on the glyoxal molecule in Chapter III shown that this equation should be accurate.

variationally by Coulson,[54] we found $(1s_H|V_{core}|1s_{He}) = -1.282$ au. For the HeH^+ calculation the energy integrals were obtained from Roothaan's formulas.[50] A crude calculation was performed on the glyoxal molecule,* with the effect of the σ-core upon the integral $(\Phi_{O_1}|V_{core}|\Phi_{C_1})$ being estimated by the use of shielding factors. The nuclear charges Z_{O_1} and Z_{C_1} were shielded by application of the Zener-Slater rules[55] to give $Z_{O_1} = +4.550$ and $Z_{C_1} = +3.25$. The nuclear charges of non-nearest neighbor nuclei, Z_{C_2} and Z_{O_2}, were shielded by assuming that the σ-electrons behave like point charges. This gave $Z_{C_2} = Z_{O_2} = +1.00$. Obviously, it was assumed that no σ-charge shift had occured. With such shielding rules, we obtained $(\Phi_{O_1}|V_{core}|\Phi_{C_1}) = -1.14$ au. These three calculations, covering three very different situations, lend strong support to the approximation $(y|V_{core}|z) = -1.00$ au.

$(x|V_{core}|z)$ is a resonance integral for non-nearest neighbor AO's. To test the approximation that $(x|V_{core}|z)$ is zero, the integral $(\Phi_{O_1}|V_{core}|\Phi_{C_2})$ was computed for glyoxal. Again the σ-core was included in the calculation by shielding. Since the overlap $S_{O_1C_2}$ is so small, the σ-core electrons should, to a good approximation, act like point charges. This requires that the shielded nuclear charges all be +1.00. With these nuclear charges, we found that $(\Phi_{O_1}|V_{core}|\Phi_{C_2}) = -0.045$ au. Since the integral is between one and two orders of magnitude smaller than the nearest-neighbor resonance integrals, it is a good approximation to neglect it. This calculation lends support to the general approximation

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* The AO basis is the same as that used in Chapter III.

that the AO resonance integrals between non-nearest neighbors are equal to zero.

In a MO calculation which explicitly includes overlap (an AO calculation), the approximations that $S_{xz} = 0$ and $(x|V_{core}|z) = 0$ produce what is called the "tight binding" approximation. This approximation has been shown to be a legitimate first approximation to calculations including all integrals.[56] One could, therefore, think of the β^{LOAO}'s derived using these approximations as "tight binding β's."

For Case C, the linear four-center example, there should be two distinct $\beta_{\mu\nu}^{LOAO}$. Derivations of these β's show that

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-1} (1 - S_{yz}^2)^{-\frac{1}{2}} [E_{yz}(EM)_{x,y} - S_{yz} S_{xy}/4], \qquad (58)$$

and that

$$\beta_{yz}^{LOAO} = (1 - S_{yz}^2)^{-1} (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{zw}^2)^{-\frac{1}{2}} [E_{xy} E_{zw}(EM)_{y,z} - S_{yz}(S_{zw} + S_{xy}) / 4]. \qquad (59)$$

The derivations may be found in Appendix I. β_{xy}^{LOAO} in the four-center case is the same as that for the three-center case. The effect upon β_{xy}^{LOAO} of other atoms in the molecule extends only to the nearest neighbors of x and y. β_{yz}^{LOAO} is analagous to β_{xy}^{LOAO} in that the same types of nearest-neighbor molecular-environmental effects are evident.

The treatment of the non-linear four-center case, Case D, produces the following equation for β_{xy}^{LOAO}:

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-1} (1 - S_{yw}^2)^{-\frac{1}{2}} (1 - S_{yz}^2)^{-\frac{1}{2}} [E_{yw} E_{yz}(EM)_{x,y} - S_{xy}(S_{yz} + S_{yw}) / 4]. \qquad (60)$$

(This derivation may also be found in Appendix I.) This is the same type of equation as was found for β_{yz}^{LOAO} in the linear four-center example. Whether each center in the resonance integral has one nearest neighbor, or one center has two nearest neighbors and the other center none, the environmental effects enter β^{LOAO} in the same way.

The great similarity in form exhibited by β^{LOAO}'s for the four cases allows one to generalize the specific results into a general equation for $\beta_{\mu\nu}^{LOAO}$. This equation may be written

$$\beta_{\mu\nu}^{LOAO} = (B_{\mu\nu}^2 \prod_{n\neq\mu,\nu} B_{\mu n} \prod_{m\neq\mu,\nu} B_{\nu m})^{-1} [\{ \prod_{m\neq\mu,\nu} E_{\mu m} \prod_{n\neq\mu,\nu} E_{\nu n}\} (EM)_{\mu,\nu} - S_{\mu\nu} \sum_{m\neq\mu,\nu} (S_{\mu m} + S_{\nu m}) / 4], \quad (61)$$

where all products Π and summations Σ are intended to range over nearest neighbors only. $B_{\mu\nu}$ and $E_{\mu m}$ are defined as

$$B_{\mu\nu} = (1 - S_{\mu\nu}^2)^{\frac{1}{2}}$$

and

$$E_{\mu m} = \{(1 + B_{\mu m}) / 2\}^{\frac{1}{2}}.$$

$B_{\mu\nu}^{LOAO}$, calculated from equation (61), is in atomic units (au).

This equation provides a relatively easy way to obtain $\beta_{\mu\nu}^{LOAO}$. One can obtain excellent approximations to the π-orbital overlaps by using the tables of Mulliken, Rieke, Orloff, and Orloff. The only term in the equation which is not readily available is the $(EM)_{\mu,\nu}$ term.

The error in the Mulliken approximation,

$$(EM)_{\mu,\nu} = (\mu|V_{core}|\nu) - (S_{\mu\nu}/2) \{(\mu|V_{core}|\mu) + (\nu|V_{core}|\nu)\}, \quad (62)$$

could be obtained for each AO pair by computing the integrals in equation

(62). This process would consume much time. A good approximation for $(EM)_{\mu,\nu}$ would be much better. Since the terms $(\mu|V_{core}|\mu)$ and $(\nu|V_{core}|\nu)$ will have to be evaluated in order to obtain α_{μ}^{LOAO} and α_{ν}^{LOAO}, a good approximation of $(\mu|V_{core}|\nu)$ in terms of these integrals would be appropriate. However, since the $(\mu|V_{core}|\nu)$ are on the order of -1.00 au and, as we shall find later, the $(EM)_{\mu,\nu}$ are on the order of -0.05 au, we are required to approximate $(\mu|V_{core}|\nu)$ to better than one per-cent accuracy. This is too difficult.

A more direct means will be taken to approximate $(EM)_{\mu,\nu}$. Integrals for the H_2 molecule are readily available for a large range of internuclear distances.[53] We also have integrals, computed using Roothaan's formulas, for a few molecules at their equilibrium internuclear distances, HeH^+, LiH, π-glyoxal, and π-H_2CO. $(EM)_{\mu,\nu}$, computed using equation (62), is plotted versus $S_{\mu\nu}$ for the H_2 molecule in figure 2. The values of $(EM)_{\mu,\nu}$ and $S_{\mu\nu}$, together with an interesting breakdown of $(EM)_{\mu,\nu}$ into kinetic and potential energy parts, are shown in Table 7. From figure 2, it appears that, for the $S_{\mu\nu}$-interval 0.500 to 0.000, $(EM)_{\mu,\nu}$ is almost exactly linear in $S_{\mu\nu}$. Now $S_{\mu\nu}$ for H_2 at its equilibrium internuclear configuration is about 0.75, and this overlap does not fall in the region of linearity. But for the π-electron systems of molecules, all the overlaps lie in this range. The assumption is made that $(EM)_{\mu,\nu}$ is linear in $S_{\mu\nu}$, provided $S_{\mu\nu}$ is less than 0.500.

The data in Table 7 shows that the part of $(EM)_{\mu,\nu}$ which is computed over the kinetic energy operator is negative. The part of $(EM)_{\mu,\nu}$ computed from the potential energy operator is positive. Since a negative $(EM)_{\mu,\nu}$ is required for binding in the H_2 molecule, these results tell us

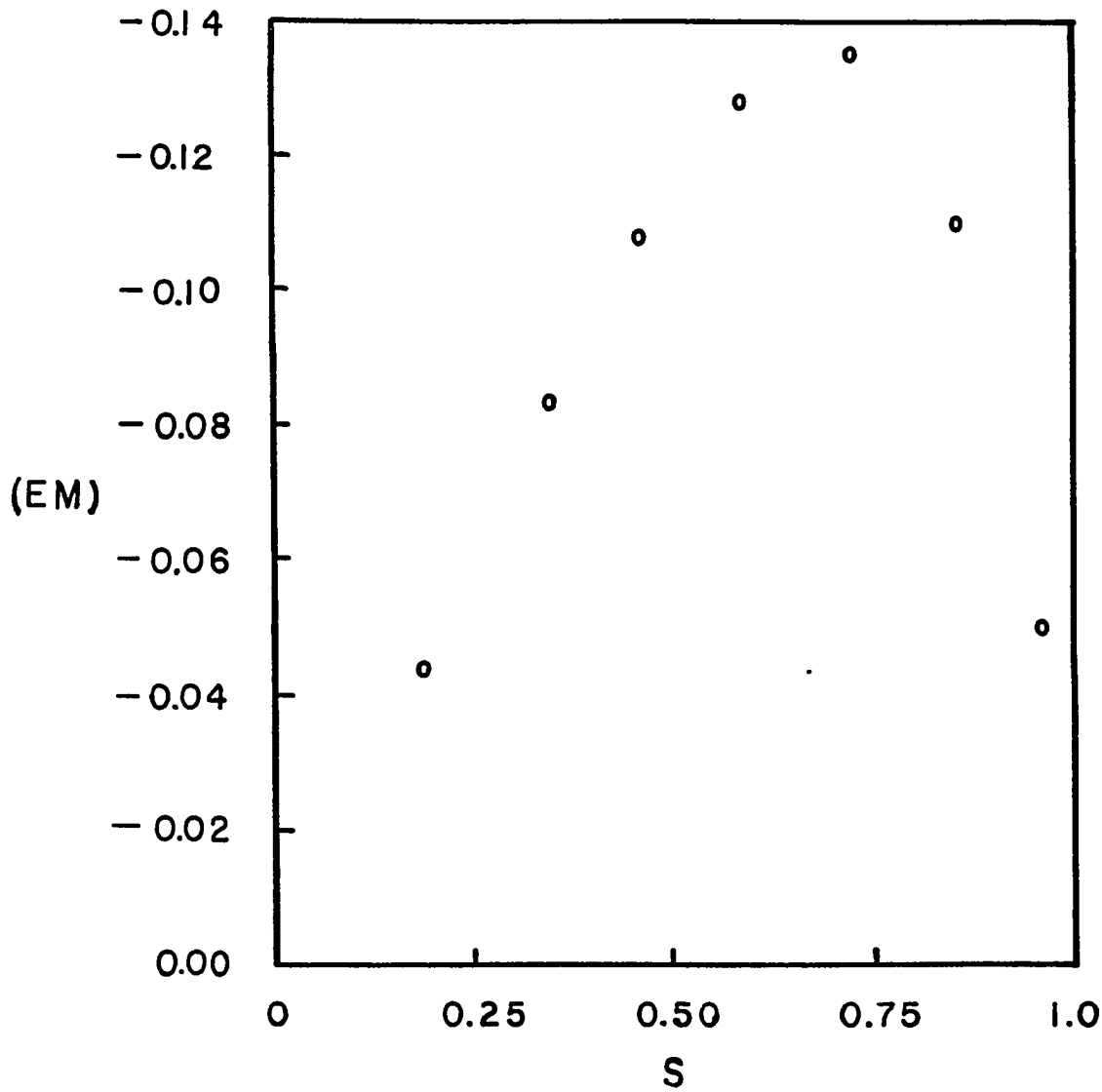


Figure 2

Error in the Mulliken approximation, (EM) in au, for the one-electron integral of H_2 plotted against the overlap S. (The orbital exponent of the 1s AO of hydrogen is 1.00.)

Table 7

The Error in the Mulliken Approximation, $(EM)_{H_1,H_2}$, for the H_2 Molecule; Its Breakdown into Kinetic Energy and Potential Energy for Several Values of the Overlap

$S_{1s_{H_1},1s_{H_2}}$ (1s orbital exponent = 1.00)	$(EM)_{H_1,H_2}$ K. E. (au)	$(EM)_{H_1,H_2}$ P. E. (au)	$(EM)_{H_1,H_2}$ (au)
0.960	-0.050	+0.001	-0.049
0.858	-0.122	+0.012	-0.110
0.725	-0.167	+0.032	-0.135
0.587	-0.181	+0.053	-0.128
0.458	-0.170	+0.062	-0.108
0.349	-0.150	+0.066	-0.084
0.189	-0.095	+0.051	-0.044

that the kinetic energy part of $(EM)_{\mu,\nu}$ provides most of the binding energy in the molecule. The potential energy part is actually destabilizing; it is also several times smaller in magnitude than the kinetic energy term. These conclusions are precisely the opposite of what would be predicted from calculation of β for an overlapping atomic orbital basis.

This appears to be the first time that such an analysis of β has been made. The conclusion that the kinetic energy is responsible for most of the binding energy in the molecule, though at first surprising, has been arrived at by a different route by Ruedenberg.[57] The fact that this binding contribution appears so dramatically in β is the surprising part. Most people have the feeling that β is determined mostly by potential energy.

It remains for us to see what factors influence the slope of the assumed linear plot of $(EM)_{\mu,\nu}$ versus $S_{\mu\nu}$. To find these factors, computed values of $(EM)_{\mu,\nu}$ (equation (62)) were compared to $S_{\mu\nu}$ for HeH^+, H_2, π-H_2CO, and LiH, all in their equilibrium configurations. $(EM)_{\mu,\nu}$ is calculated over the kinetic energy operator and nucleus-electron-attraction potential operator of the Hartree-Fock effective Hamiltonian. Where a core of σ-electrons is present, this core is not included in the calculations. Studies have shown that the σ-core will have very little effect upon $(EM)_{\mu,\nu}$.[36] (This statement does not strictly apply to the part of V_{core} which contains the electronic permutation operator $\tilde{P}_{1,2}$. This part of V_{core} introduces σ-π exchange. There are some electron-repulsion integrals introduced into $\beta_{\mu\nu}^{LOAO}$ by the σ-π exchange effect, which, though small, are non-zero. These integrals are of the type

$(\phi_\nu(1)\ \phi_\nu^\sigma(1) \mid \phi_\mu(2)\ \phi_\mu^\sigma(2))$, where ϕ_ν^σ and ϕ_μ^σ are σ-LOAO's on atomic centers ν and μ respectively. These integrals show little of the type of overlap coupling effect found in $(EM)_{\mu,\nu}$, and, to a good approximation, they may be considered apart from the treatment of $(EM)_{\mu,\nu}$.) The comparisons of $(EM)_{\mu,\nu}$ and $S_{\mu\nu}$ are shown in figure 3, where straight lines are drawn connecting the $(EM)_{\mu,\nu}$ with the origin of the graph. The lines are extrapolated to S = 0.500, thereby covering the region of assumed linearity.

The slopes of the lines in figure 3 are obviously very different. However, some general relationships may be inferred. It appears that the larger the difference between the orbital exponents of the AO's ϕ_μ and ϕ_ν used to compute $(EM)_{\mu,\nu}$, the greater the error in the Mulliken approximation. There also appears to be a dependence upon the sum of the orbital exponents, the greater the sum the greater $(EM)_{\mu,\nu}$. Based upon this admittedly small sampling of data, a guess can be made as to the form for $(EM)_{\mu,\nu}$. The guess is that $(EM)_{\mu,\nu}$ can be expressed by the following equation:

$$(EM)_{\mu,\nu} = -\kappa^i S_{\mu\nu} \{1 + |\xi_\mu - \xi_\nu|\} (\xi_\mu + \xi_\nu) / 2, \qquad (63)$$

where

κ^i is a constant depending upon whether the orbitals are $\sigma(i = \sigma)$ or $\pi(i = \pi)$,

and

$|\xi_\mu - \xi_\nu|$ is the absolute value of the difference in orbital exponents of the AO's μ and ν.

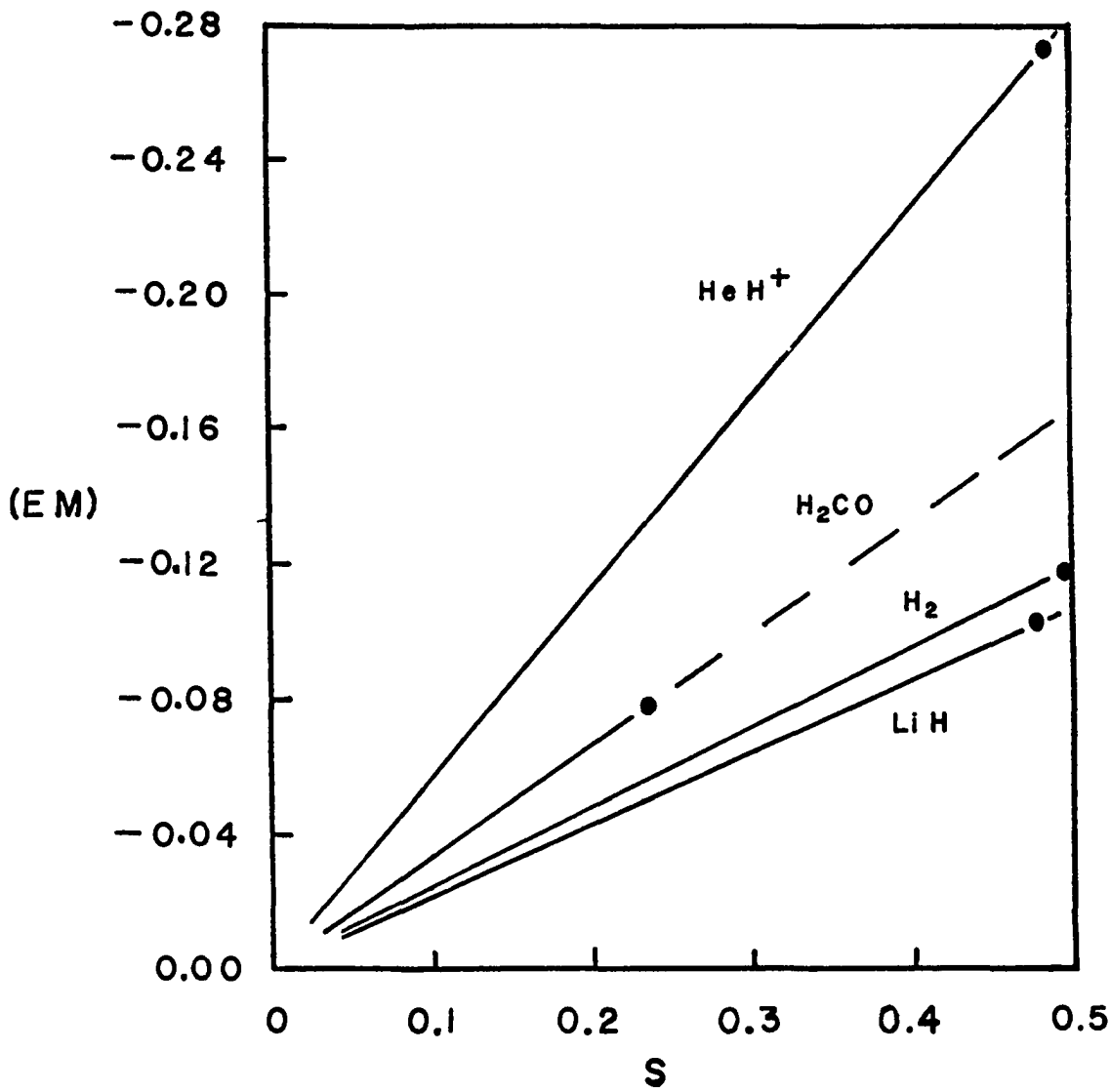


Figure 3

Error in the Mulliken approximation, (EM) in au, for the one-electron integrals of HeH^+, π-H_2CO, H_2, and LiH plotted against the overlap S. Dots on the heteronuclear plots correspond to values at the equilibrium configuration. (The orbital exponents for the AO pairs are as follows: HeH^+, 1.87, 0.722; H_2CO, 1.57, 2.23; H_2, 1.00; LiH, 0.658, 1.00.)

Based upon the sole point in figure 3 for π-systems, that for H_2CO, a value of 0.112 is chosen for κ^{π}. For σ-systems, the appropriate value for κ^{σ} is roughly double what it is for π-systems, $\kappa^{\sigma} = 0.211$. This value of κ^{σ} will reproduce the actual $(EM)_{\mu,\nu}$, for the molecules H_2, HeH^+, and LiH, to within 10%.

Of course for this π-electron development, the only form for $(EM)_{\mu,\nu}$ which will be used is that form with κ^{π}. Therefore, we may restrict our attention to the equation

$$(EM)_{\mu,\nu} = -0.112\ S_{\mu\nu}\ \{1 + |\xi_\mu - \xi_\nu|\}\ (\xi_\mu + \xi_\nu)\ /\ 2. \qquad (64)$$

This equation relates $(EM)_{\mu,\nu}$ to a specific AO basis through both the overlap and the orbital exponent factor. In order to calculate with such an equation, it is necessary to specify that AO basis. The basis set which will be used in this work is a minimum set of STO's with orbital exponents determined variationally by Roothaan for the isolated atoms.[58] The orbital exponents for these best atom AO's, for the atoms C, N, and O, are listed in Table 8.

Once we have specified a basis set of π-AO's, we can calculate the orbital exponent factors in equation (64). For the atoms C, N, and O the factors have been calculated, with the term -0.112 being absorbed, and are listed in Table 9. The factors $K_{\mu\nu}$ are given by the equation

$$K_{\mu\nu} = -0.112\ \{1 + |\xi_\mu - \xi_\nu|\}\ (\xi_\mu + \xi_\nu)\ /\ 2. \qquad (65)$$

$K_{\mu\nu}$ may now be substituted into equation (64) to obtain the simpler equation

$$(EM)_{\mu,\nu} = K_{\mu\nu}\ S_{\mu\nu}. \qquad (66)$$

For a given AO pair, μ and ν, $(EM)_{\mu,\nu}$ is related only to the overlap.

Table 8

Orbital Exponents for Best Atom Atomic Orbitals.[a,b]

Atomic Orbital	Carbon	Nitrogen	Oxygen	Hydrogen
1s	5.673	6.665	7.658	1.000
2s	1.608	1.924	2.246	
$2p_\sigma$	1.568	1.917	2.226	
$2p_\pi$	1.568	1.917	2.226	

a) Reference 58.

b) For purposes of comparison, the Slater orbital exponents for 2s and 2p of C, N, and O are, respectively, 1.625, 1.950, and 2.275.

Table 9

The $K_{\mu\nu}$ Parameter

Atom Pair (μ, ν)	$K_{\mu\nu}$
N, N	-0.215
O, O	-0.249
C, C	-0.176
N, O	-0.304
N, C	-0.263
O, C	-0.352

For additional proof of the validity of the equation for $(EM)_{\mu,\nu}$, we calculate the $(EM)_{\mu,\nu}$ for ethylene using equation (65). This $(EM)_{\mu,\nu}$ and the overlap $S_{\mu\nu}$ are used to calculate $\beta_{\mu\nu}^{LOAO}$ for ethylene. Such a calculation produces a $\beta_{\mu\nu}^{LOAO}$ of -0.056 au. Cook, Hollis, and McWeeny computed a $\beta_{\mu\nu}^{LOAO}$ for ethylene of -0.05 au.[36] They used accurate methods, comparable to a calculation using equation (62). Considering that they do not report a third decimal place, the agreement between the two values for β is satisfactory. This comparison provides additional evidence for the choice made for κ^{π}.

For the simple two-center case, Case A, this development gives us a simple form for $\beta_{\mu\nu}^{LOAO}$. This form is

$$\beta_{\mu\nu}^{LOAO} = (1 - S_{\mu\nu}^2)^{-1} K_{\mu\nu} S_{\mu\nu}. \qquad (67)$$

However, for the polyatomic molecule with a V_{core} which includes potential terms due to atoms other than μ and ν, one wonders how applicable the preceding development really is. In the multi-center case, $(EM)_{\mu,\nu}$ contains not only the error in the Mulliken approximation for the two-center integrals over the μ and ν contributions to V_{core}, but also the error in the Mulliken approximation for the three-center integrals, which appear because of other atoms included in V_{core}. For π-systems, there are two factors which minimize the importance of these three-center contributions to $(EM)_{\mu,\nu}$. First, the H_2 example shows that kinetic energy terms are the largest contributors to $(EM)_{\mu,\nu}$. The kinetic energy terms are at most two-centered. Second, calculations involving three hydrogen atoms,[59] at internuclear distances where the overlap between the hydrogen 1s orbitals is on par with π-overlaps, show that the error in the Mulliken approximation for three-center potential energy integrals is from four to six times

less than the error in the Mulliken approximation for two-center integrals (two-center in Table 7). These arguments minimize the importance of the three-center potential energy integrals in determining $(EM)_{\mu,\nu}$. Therefore $(EM)_{\mu,\nu}$ is approximately the same for a poly-center molecule as it would be for a two-center molecule, given that the overlaps $S_{\mu\nu}$ are the same in both cases. Formally ignoring the three-center integrals over AO's in the $\beta_{\mu\nu}^{LOAO}$ terms for poly-center molecules is equivalent to saying that such integrals are approximated to acceptable accuracy by the Mulliken approximation.

Having determined $(EM)_{\mu,\nu}$ as a function of $S_{\mu\nu}$ and $K_{\mu\nu}$, we may now write the equation for $\beta_{\mu\nu}^{LOAO}$ as follows:

$$\beta_{\mu\nu}^{LOAO} = S_{\mu\nu}(B_{\mu\nu}^{2} \prod_{n\neq\mu,\nu} B_{\mu n} \prod_{m\neq\mu,\nu} B_{\nu m})^{-1} [\{ \prod_{m\neq\mu,\nu} E_{\mu m} \prod_{n\neq\mu,\nu} E_{\nu n}\} K_{\mu\nu} - \sum_{m\neq\mu,\nu} (S_{\mu m} + S_{\nu m}) / 4]. \quad (68)$$

This equation gives $\beta_{\mu\nu}^{LOAO}$ as the product of the overlap $S_{\mu\nu}$ and a term which collects the effects of the local molecular environment.

(2) Derivation of α_{μ}^{LOAO}

We derive the α_{μ}^{LOAO}, defined by equation (47),

$$\alpha_{\mu}^{LOAO} = (\phi_{\mu}(1)|V_{core}|\phi_{\mu}(1)),$$

for the same four cases as in the derivation of $\beta_{\mu\nu}^{LOAO}$ (see figure 1). We use the same sets of LOAO's for each case, and, since we have written these sets in deriving $\beta_{\mu\nu}^{LOAO}$, we shall not reproduce them here.

For the two-AO case, Case A, one substitutes the AO-expansion for

ϕ_x into equation (47) and obtains

$$\alpha_x^{LOAO} = (1 - S_{xy}^2)^{-1} \{E_{xy}^2 (x|V_{core}|x) + (S_{xy}^2/4E_{xy}^2)\ (y|V_{core}|y) - S_{xy}(x|V_{core}|y)\}. \quad (69)$$

This equation gives α_x^{LOAO} in terms of the overlap S_{xy}, the integrals $(x|V_{core}|x)$ and $(y|V_{core}|y)$, and the resonance integral $(x|V_{core}|y)$. The calculation of the first three of these terms, though tedious, is straightforward. $(x|V_{core}|y)$ is more difficult to calculate and will be approximated. For now, we shall not simplify equation (69) further.

For the three-AO case, Case B, one needs to derive both α_x^{LOAO} and α_y^{LOAO}. The AO expansions for ϕ_x and ϕ_y' are substituted into equation (47) with the following results:

$$\alpha_x^{LOAO} = (1 - S_{xy}^2)^{-1} \{E_{xy}^2 (x|V_{core}|x) + (S_{xy}^2/4E_{xy}^2)\ (y|V_{core}|y) - S_{xy}(x|V_{core}|y)\}, \quad (70)$$

and

$$\alpha_y^{LOAO} = (1 - S_{y',z}^2)^{-1} \{E_{y',z}^2 (\phi_y|V_{core}|\phi_y) + (S_{y',z}^2/4E_{y',z}^2)\ (z|V_{core}|z) - S_{y',z}(\phi_y|V_{core}|z)\}. \quad (71)$$

α_x^{LOAO} has the same form in this three-AO example that it had for Case A. One can conclude that an α^{LOAO} is influenced only by the local molecular environment, i.e. nearest neighbors. This is consistent with the environmental behavior of $\beta_{\mu\nu}^{LOAO}$.

The approximations which we make in order to simplify α_y^{LOAO} are the same as those made in simplifying the β^{LOAO}'s. One can approximate $S_{y',z}$

by

$$S_{y'z} = (1 - S_{xy}^2)^{-\frac{1}{2}} E_{xy} S_{yz},$$

or by

$$S_{y'z} = S_{yz}.$$

Wherever $S_{y'z}^2$ is compared to unity, i.e. in $(1 - S_{y'z}^2)$, the second approximation is used. Where $S_{y'z}$ stands alone, the first approximation is used. Where LOAO's appear in the energy integrals, we expand them in AO's. Such expansions give

$$(\phi_y|V_{core}|\phi_y) = (1 - S_{xy}^2)^{-1} \{E_{xy}^2(y|V_{core}|y) + (S_{xy}^2/4E_{xy}^2)\ (x|V_{core}|x) - S_{xy}(x|V_{core}|y)\},$$

and

$$(\phi_y|V_{core}|z) = (1 - S_{xy}^2)^{-\frac{1}{2}} \{E_{xy}(y|V_{core}|z) - (S_{xy}/2E_{xy})\ (x|V_{core}|z)\}.$$

With the approximation that $(x|V_{core}|z) = 0$, $(\phi_y|V_{core}|z)$ becomes

$$(\phi_y|V_{core}|z) = (1 - S_{xy}^2)^{-\frac{1}{2}} E_{xy}(y|V_{core}|z).$$

Substituting these approximations into equation (71) and simplifying, we obtain

$$\alpha_y^{LOAO} = (1 - S_{yz}^2)^{-1} (1 - S_{xy}^2)^{-1} \{E_{yz}^2\ E_{xy}^2(y|V_{core}|y) + (E_{yz}^2\ S_{xy}^2/4E_{xy}^2)\ (x|V_{core}|x) + (E_{xy}^2\ S_{yz}^2/4E_{yz}^2)\ (z|V_{core}|z) - E_{yz}^2\ S_{xy}(x|V_{core}|y) - E_{xy}^2\ S_{yz}(y|V_{core}|z)\}. \quad (72)$$

We do not employ the approximation $(x|V_{core}|y) = (y|V_{core}|z) = -1.00$ au

used in deriving $\beta_{\mu\nu}^{LOAO}$. In the equations for $\beta_{\mu\nu}^{LOAO}$ these integrals were multipliers of factors on the order of S^2. Here, the integrals multiply factors on the order of S. Therefore, unacceptable error would occur if this approximation were used in equation (72). We shall approximate these integrals using more accurate methods.

Within the accuracy allowed by the approximate nature of the LOAO's used here, an α^{LOAO} is independent of the molecular environment, save nearest neighbors. Therefore, the linear four-AO example, Case C, will provide no new information regarding a general equation for α_{μ}^{LOAO}. The equations derived for α_{x}^{LOAO} and α_{y}^{LOAO} for Case B are applicable to the linear four-center case.

The non-linear four-center case, Case D, does provide some unique information. No approximation techniques beyond those for Case B are used. The results of these derivations, carried out with the same LOAO set as was used to obtain the β^{LOAO}'s for this case, are as follow :

$$\alpha_x^{LOAO} = (1 - S_{xy}^2)^{-1} \{E_{xy}^2 (x|V_{core}|x) + (S_{xy}^2/4E_{xy}^2)\ (y|V_{core}|y) - S_{xy}(x|V_{core}|y)\}, \tag{73}$$

and

$$\alpha_y^{LOAO} = (1 - S_{yw}^2)^{-1}\ (1 - S_{yz}^2)^{-1}\ (1 - S_{xy}^2)^{-1} \{E_{yz}^2\ E_{xy}^2\ E_{yw}^2 (y|V_{core}|y) + (E_{yw}^2\ E_{yz}^2\ S_{xy}^2/4E_{xy}^2)\ (x|V_{core}|x) + (E_{xy}^2\ E_{yw}^2\ S_{yz}^2/4E_{yz}^2)\ (z|V_{core}|z) + (E_{yz}^2\ E_{xy}^2\ S_{yw}^2/4E_{yw}^2)\ (w|V_{core}|w) - E_{yw}^2\ E_{yz}^2\ S_{xy}(x|V_{core}|y) - E_{yw}^2\ E_{xy}^2\ S_{yz}(y|V_{core}|z) - E_{xy}^2\ E_{yz}^2\ S_{yw}(y|V_{core}|w)\}. \tag{74}$$

The derivations of these terms may be found in Appendix II. As expected,

α_x^{LOAO}, with only one nearest neighbor, has the same form as that found in Case B.

The great similarities between the equations derived for α_μ^{LOAO} in the specific examples allow one to generalize the results. The general equation for α_μ^{LOAO} is

$$\alpha_\mu^{LOAO} = \Big(\prod_{n\neq\mu} B_{\mu n}\Big)^{-2} \Big[\Big(\prod_{n\neq\mu} E_{\mu n}^2\Big)(\mu|V_{core}|\mu) + \sum_{n\neq\mu}\Big\{\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2/(4E_{\mu n}^2)\Big\}(n|V_{core}|n) - \sum_{n\neq\mu}\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}(\mu|V_{core}|n)\Big], \tag{75}$$

where all summations Σ and products Π are over nearest neighbors to μ only. $B_{\mu n}$ and $E_{\mu n}$ are defined here in the same way that they were defined for equation (61).

In order to calculate α_μ^{LOAO} with equation (75), we must calculate not only the overlap matrix for the molecule, but also integrals of the types $(n|V_{core}|n)$ and $(\mu|V_{core}|n)$. We can simplify equation (75) by approximating $(\mu|V_{core}|n)$ in terms of integrals $(n|V_{core}|n)$. When this simplification is completed, the formal derivation of α_μ^{LOAO} is finished.

In deriving an equation for $\beta_{\mu\nu}^{LOAO}$, we found that $(EM)_{\mu,\nu}$ could be expressed in two ways. The first was an exact expression and the second an approximation to this exact expression. These two equations (equations (62) and (66) respectively) are

$$(EM)_{\mu,\nu} = (\mu|V_{core}|\nu) - (S_{\mu\nu}/2)\{(\mu|V_{core}|\mu) + (\nu|V_{core}|\nu)\},$$

and

$$(EM)_{\mu,\nu} = K_{\mu\nu} S_{\mu\nu}.$$

Since equation (66) provides a good approximation to $(EM)_{\mu,\nu}$, we equate the two expressions and solve for $(\mu|V_{core}|\nu)$. We obtain

$$(\mu|V_{core}|\nu) = S_{\mu\nu} [\frac{1}{2} \{(\mu|V_{core}|\mu) + (\nu|V_{core}|\nu)\} + K_{\mu\nu}]. \quad (76)$$

This equation shows the relationship between formal no-overlap MO theories and MO theories which include the overlap. A good approximation for $(EM)_{\mu,\nu}$ automatically implies a good approximation for $(\mu|V_{core}|\nu)$. We have obtained an approximation for $(\mu|V_{core}|\nu)$ which maintains the original form for the Mulliken approximation but which improves it by adding a correction term.

Although the AO resonance integral $(\mu|V_{core}|\nu)$ is taken over the total V_{core}, including the σ-electrons, $K_{\mu\nu}$ was obtained earlier using only the kinetic energy and nuclear-framework-potential of the Hartree-Fock operator. This underlines the point made earlier, that the Mulliken approximation adequately takes account of the effects in $(\mu|V_{core}|\nu)$ due to σ-electrons (with the exception of σ-π exchange effects caused by the presence of the $\tilde{P}_{1,2}$ operator in V_{core}). The error in the Mulliken approximation is due almost solely to the error for integrals taken over the kinetic energy and nuclear-framework-potential operators.

Equation (76) may be used to simplify the general equation for α_μ^{LOAO}. The substitution of the approximate expression for $(\mu|V_{core}|n)$ into equation (75) gives

$$\alpha_\mu^{LOAO} = \left(\prod_{n\neq\mu} B_{\mu n}\right)^{-2} \left[\left\{\left(\prod_{n\neq\mu} E_{\mu n}^2\right) - \sum_{n\neq\mu}\left(\prod_{m\neq n,\mu} E_{\mu m}^2\right) S_{\mu n}^2/2\right\} (\mu|V_{core}|\mu)\right.$$

$$+ \sum_{n\neq\mu}\left\{\left(\prod_{m\neq n,\mu} E_{\mu m}^2\right) S_{\mu n}^2 \{(1/2E_{\mu n}^2) - 1\} / 2\right\} (n|V_{core}|n)$$

$$\left. - \sum_{n\neq\mu}\left(\prod_{m\neq n,\mu} E_{\mu m}^2\right) S_{\mu n}^2 K_{\mu n}\right] \qquad (77)$$

This expression for α_μ^{LOAO} couples the AO integral $(\mu|V_{core}|\mu)$ to its nearest neighbors. This coupling occurs through the elements of the overlap matrix $\underset{\sim}{S}$.

(C) Testing the Approximate Equations for α_μ^{LOAO} and $\beta_{\mu\nu}^{LOAO}$

The α_μ^{LOAO} and $\beta_{\mu\nu}^{LOAO}$ have been calculated in Chapter III for the glyoxal molecule. These calculations were done using the kinetic energy and nucleus-electron-attraction part of V_{core} only. The values of α_C^{LOAO} and α_O^{LOAO}, and $\beta_{C_1O_1}^{LOAO}$ and $\beta_{C_1C_2}^{LOAO}$, computed in this chapter, are given in Table 10.

We have computed these same terms with the approximate equations (equations (68) and (77)), and the values of these terms are also listed in Table 10. All integrals in the approximate equation for α_μ^{LOAO} of the type $(i|V_{core}|i)$ were calculated over the kinetic energy and nucleus-electron-attraction part of V_{core} only. The β^{LOAO}'s and α^{LOAO}'s computed using the approximate equations are generally slightly larger than the α^{LOAO}'s and β^{LOAO}'s of Chapter III. This slight difference is to be expected. The reason for it is that some approximations were made in deriving equations (68) and (77) based upon there being a σ-core of

Table 10

A Comparison of Approximate Calculations of α_{μ}^{LOAO} and $\beta_{\mu\nu}^{LOAO}$ to Accurate Calculations of α_{μ}^{LOAO} and $\beta_{\mu\nu}^{LOAO}$ for the Glyoxal Molecule

Integral	Approximate Value (au)	Calculated Value (au) Option A Atomic Functions[a]	Calculated Value (au) Option B Atomic Functions[a]
α_{O}^{LOAO}	-11.438	-11.441	-11.447
α_{C}^{LOAO}	-10.354	-10.345	-10.338
β_{CO}^{LOAO}	- 0.101	- 0.102	- 0.095
β_{CC}^{LOAO}	- 0.072	- 0.064	- 0.058

a) The two options refer to the two possible choices in the initial pair in the orthogonalization process.

electrons. The approximations were that $(x|V_{core}|z) = 0$ if x and z are not nearest neighbors and that $(x|V_{core}|y) = -1.00$ au. if x and y are nearest neighbors. These approximations cause the α^{LOAO}'s and β^{LOAO}'s to be slightly larger than if the approximations were not made and the integrals actually computed over the part of V_{core} used in Chapter III. For calculations on actual molecules, which do have σ-cores, the approximate equations show the correct behavior. The fact that the β^{LOAO}'s computed with the approximate equations have values which are close to the values of the β^{LOAO}'s computed in Chapter III supports the contention that, beyond the effect of σ-π exchange, β^{LOAO}'s are not influenced much by the σ-core.

(D) Further Approximation of α_μ^{LOAO}

The operator V_{core} has earlier been written

$$V_{core} = -\frac{1}{2}\nabla_1^2 - \sum_A V_A(1) + \sum_{\lambda,\sigma'}^{\substack{occ.\ \sigma \\ MO's}} P_{\lambda\sigma'}^{LOAO} \{\phi_\lambda(1)\ \phi_{\sigma'}(2) - \frac{1}{2}\phi_\lambda(2)\ \tilde{P}_{1,2}\ \phi_{\sigma'}(2)\}.$$

We can write this operator formally as

$$V_{core} = (V_{core})_\mu + \sum_{j\neq\mu} (V_{core})_j, \tag{78}$$

where $(V_{core})_\mu$ contains the kinetic energy, the nucleus-electron attraction, and the effect of the σ-core of atom μ. $(V_{core})_j$ contains the sum of the nucleus-electron attraction and σ-core repulsions of atom j.

Introduction of this decomposition for V_{core} into the integral

$(\mu|V_{core}|\mu)$ gives

$$(\mu|V_{core}|\mu) = (\mu|(V_{core})_\mu|\mu) + (\mu| \sum_{j\neq\mu} (V_{core})_j|\mu). \qquad (79)$$

This equation gives the interaction of an electron in the μ π-orbital with the total core as the sum of a μ π-electron, μ core interaction and a term which accounts for the coulombic interactions of the other cores in the molecule.

We shall make a further decomposition of V_{core}. We can write

$$V_{core} = (V_{core})_\mu + \sum_{\ell\neq\mu} (V_{core})_\ell + \sum_{m\neq\mu} (V_{core})_m, \qquad (80)$$

where the summation over ℓ includes nearest-neighbors-to-μ which have π-electrons, and the summation over m includes all atoms except nearest-neighbors-to-μ and all atoms which bear no π-electrons. Substituting this V_{core} into $(\mu|V_{core}|\mu)$ produces

$$(\mu|V_{core}|\mu) = (\mu|(V_{core})_\mu|\mu) + (\mu| \sum_{\ell\neq\mu} (V_{core})_\ell|\mu) + (\mu| \sum_{m\neq\mu} (V_{core})_m|\mu). \qquad (81)$$

Another way to write this equation is

$$(\mu|V_{core}|\mu) = (\mu|(V_{core})_{local}|\mu) + (\mu| \sum_{m\neq\mu} (V_{core})_m|\mu), \qquad (82)$$

where $(V_{core})_{local}$ includes the μ atom and its π-electron bearing nearest neighbors.

Where equation (82) is used to expand the terms $(\mu|V_{core}|\mu)$ in equation (77), the second term of equation (82) will be "factored out" of

the equation. The integrals $(n|V_{core}|n)$ will be computed over the local core operator only. Equation (77) then becomes

$$\alpha_\mu^{LOAO} = \Big(\prod_{n\neq\mu} B_{\mu n}\Big)^{-2} \Big[\Big\{\Big(\prod_{n\neq\mu} E_{\mu n}^2\Big) - \sum_{n\neq\mu}\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2/2\Big\}(\mu|(V_{core})_{local}|\mu) + \sum_{n\neq\mu}\Big\{\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2\{(1/2E_{\mu n}^2) - 1\}/2\Big\}(n|(V_{core})_{local}|n) - \sum_{n\neq\mu}\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2 K_{\mu n}\Big] + (\mu|\sum_{\substack{m\neq\mu \\ m\neq \text{nearest } \pi\text{-bearing} \\ \text{neighbors-to-}\mu}} (V_{core})_m|\mu). \tag{83}$$

We make this approximation in order to emphasize the local nature of the overlap-coupling effect. The μ orbital is coupled only to its nearest neighbors by overlap. The non-nearest neighbors which have π-electrons and all atoms which are not a part of the π-system affect α_μ^{LOAO} only through the electrostatic interactions of their cores.

Whether α_μ^{LOAO} is computed with equation (77), utilizing the full V_{core}, or with equation (83), using $(V_{core})_{local}$ inside the overlap-coupled part of α_μ^{LOAO} and adding on the effect of other atoms, one obtains to a good approximation the same result. This is to be expected if the Mulliken approximation adequately takes account of the three-center integrals introduced by non-nearest neighbors. Since equation (77) was derived under this assumption, it is consistent to take the step which leads to equation (83).

In order to calculate the $(i|(V_{core})_j|i)$ we need to write out

$(V_{core})_j$ in more specific terms. If j = i, then we have

$$(V_{core})_i = -\frac{1}{2}\nabla_1^2 - V_i(1) + \sum_{\substack{\lambda,\sigma' \\ \text{(LOAO's on i)}}}^{\substack{occ.\ \sigma \\ MO's}} P^{LOAO}_{\lambda\sigma'} \left(\phi_\lambda(2)\ \phi_{\sigma'}(2) - \frac{1}{2}\phi_\lambda(2)\ \tilde{P}_{1,2}\ \phi_{\sigma'}(2)\right). \quad (84)$$

If $j \neq i$, then we have

$$(V_{core})_j = V_j(1) + \sum_{\substack{\lambda,\sigma' \\ \text{(LOAO's on j)}}}^{\substack{occ.\ \sigma \\ MO's}} P^{LOAO}_{\lambda\sigma'} \left(\phi_\lambda(2)\ \phi_{\sigma'}(2) - \frac{1}{2}\phi_\lambda(2)\ \tilde{P}_{1,2}\ \phi_{\sigma'}(2)\right). \quad (85)$$

To facilitate the calculation of $(i|(V_{core})_i|i)$, we assume that the electron density $\phi_\lambda(2)\ \phi_{\sigma'}(2)$ on i does not interact with the π-density i(1)i(1) unless $\lambda = \sigma'$. If $\lambda = \sigma'$ then the density $\phi_\lambda(2)\phi_\lambda(2)$ interacts as though the interaction were computed with AO's instead of LOAO's. The density is, therefore, written $\lambda(2)\ \lambda(2)$. The exchange operator $-\frac{1}{2}\phi_\lambda(2)\ \tilde{P}_{1,2}\ \phi_{\sigma'}(2)$ will likewise interact only if $\lambda = \sigma'$, and its interaction is assumed to be given by AO's instead of LOAO's. We therefore write an approximation to equation (84)

$$(V_{core})_i = -\frac{1}{2}\nabla_1^2 - V_i(1) + \sum_{\substack{\lambda=\sigma \\ \text{AO's on i}}} P^{LOAO}_{\lambda\lambda} \left(\lambda(2)\ \lambda(2) - \frac{1}{2}\lambda(2)\ \tilde{P}_{1,2}\ \lambda(2)\right). \quad (86)$$

To facilitate calculation of $(i|(V_{core})_j|i)$, we assume that the electron density $\phi_\lambda(2)\ \phi_{\sigma'}(2)$ on j does not interact with the density

i(1) i(1) unless $\lambda = \sigma'$. If $\lambda = \sigma'$ then the density $\phi_\lambda(2)\ \phi_\lambda(2)$ interacts as though it were the AO density $\lambda(2)\ \lambda(2)$. We assume that the exchange operator $-\frac{1}{2}\phi_\lambda(2)\ \tilde{P}_{1,2}\ \phi_{\sigma'}(2)$ does not interact with the density i(1)i(1). Therefore, we write an approximation to equation (85) as

$$(V_{core})_j = -V_j(1) + \sum_{\substack{\lambda=\sigma \\ \text{AO's on j}}} P^{LOAO}_{\lambda\lambda}\ \lambda(2)\ \lambda(2). \tag{87}$$

When we substitute equation (86) into $(i|(V_{core})_i|i)$ we obtain

$$(i|(V_{core})_i|i) = (i(1)|\ -\tfrac{1}{2}\nabla_1^2|i(1)) + (i(1)|\ -V_i(1)|i(1))$$

$$+ \sum_{\substack{\lambda=\sigma \\ \text{AO's on i}}}^{\substack{occ.\ \sigma \\ MO's}} P^{LOAO}_{\lambda\lambda}\ (i(1)\ i(1)|\lambda(2)\ \lambda(2)) - \frac{1}{2}\sum_{\substack{\lambda=\sigma \\ \text{AO's on i}}} P^{LOAO}_{\lambda\lambda}\ (i(i)\ \lambda(1)|i(2)\ \lambda(2)). \tag{88}$$

When we substitute equation (87) into $(i|(V_{core})_j|i)$ we have

$$(i|(V_{core})_j|i) = (i(1)|\ -V_j(1)|i(1)) + \sum_{\substack{\lambda=\sigma \\ \text{AO's on j}}} P^{LOAO}_{\lambda\lambda}\ (i(1)\ i(1)|\lambda(2)\ \lambda(2)). \tag{89}$$

In order to derive equations (88) and (89), we set certain LOAO density functions equal to zero and set other LOAO density functions equal to functions over the corresponding AO's. The work of Cook, Hollis, and McWeeny indicates that the LOAO densities which we have set equal to zero are indeed negligible. Setting the remaining LOAO densities equal to AO densities is, however, not strictly justified by their work. To strictly justify this approximation, we shall have to rely upon the quality

of the results produced by calculations with the overall method.

We may, however, provide some qualitative justification for this approximation. Cook, Hollis, and McWeeny concluded that one-center LOAO integrals of the form $(\phi_i^A \phi_i^A \mid \phi_i^A \phi_i^A)$ should be about 9 to 14% larger than the electron-repulsion integrals calculated over the corresponding AO's. They concluded that two-center LOAO integrals of the form $(\phi_i^A \phi_i^A \mid \phi_k^B \phi_k^B)$ should be about 9 to 14% smaller than the integrals computed over the corresponding AO's, provided that A and B are nearest neighbors.* Since an atom in a π-system will have more nearest-neighbor integrals than one-center integrals, these conclusions indicate that the electron-repulsions calculated over LOAO's would be a per cent or so smaller than the electron-repulsions calculated over AO's. With our approximation of the LOAO density $\phi_\lambda(2)\ \phi_\lambda(2)$ by the AO density $\lambda(2)\ \lambda(2)$ and substitution of the resulting approximate equations for $(i|(V_{core})_i|i)$ and $(i|(V_{core})_j|i)$ (equations (88) and (89)) into the equation for α_i^{LOAO}, we do achieve a slight decrease in the electron-repulsions calculated over the AO's. Qualitatively, our approximations are in the right direction. Also, it is mathematically incorrect to include the one-center exchange integrals $(i(1)\ \lambda(1) \mid i(2)\ \lambda(2))$ in equation (88) and then substitute equation (88) into the equation for α_i^{LOAO}. These exchange integrals have about the same value calculated over the AO basis as if calculated over the LOAO basis. However, as Cook, Hollis, and McWeeny point out, these

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* These conclusions must apply only to integrals involving interactions of π-electrons with σ-electrons and σ-electrons with σ-electrons. Parr (reference 22) has shown that the LOAO integrals are almost exactly equal to the AO integrals for π-electrons interacting with π-electrons.

integrals are small. Including them in equation (88) provides much simplification and little error.

For equations (88) and (89), we can calculate the kinetic energy integrals, the nucleus-electron-attraction integrals, and the electron-repulsion integrals with Roothaan's formulas.[50] We must approximate the $P_{\lambda\lambda}^{LOAO}$ in some fashion. Once these things have been done, we can calculate the $(i|(V_{core})_i|i)$ and $(i|(V_{core})_j|i)$, substitute them into equation (83), and calculate α_i^{LOAO}.

(1) Further Approximation of $(i|(V_{core})_i|i)$ and $(i|(V_{core})_j|i)$

We could calculate the $(i|(V_{core})_i|i)$ interactions by assuming some $P_{\lambda\lambda}^{LOAO}$ and calculating all the necessary integrals from Roothaan's formulas for each molecule. But it would simplify things to assume values for the $P_{\lambda\lambda}^{LOAO}$, to compute the parts of equation (88) over a specific AO basis, and to sum these terms to give an $(i|(V_{core})_i|i)$ for each atom of a π-system. We have done this for the atoms carbon, nitrogen, and oxygen for the "best atom" AO's defined by the data in Table 8. The results are listed in Table 11.

Table 11 gives the sum of the first two terms of equation (88) in column one. In column two, we give the total σ-core repulsion seen by a π-electron. We compute the entries of column two assuming that the $P_{\lambda\lambda}^{LOAO}$ are well approximated by the orbital populations of isolated atoms. We assume that the σ-AO's are sp^2 hybridized and that the populations of the three sp^2 hybrids are all equal. We assume the promotion of one 2s electron to the 2p subshell for carbon, and we assume no s-p promotion for oxygen and nitrogen. We obtained values for the electronic repulsion

Table 11

Some Integrals Used in the Calculation of the Interaction of a π-Electron with Its Own Core

Atom	Nucleus-Electron Attraction Plus Kinetic Energy (au)	π, σ-core Repulsions (au)	Total (au)
C	-3.474	3.220	-0.254
N	-4.873	4.646	-0.227
O	-6.426	6.169	-0.257

integrals from the tables of Sahni and Cooley.[60] Column three of Table 11 shows the sum of the first three terms of equation (88). One would expect the magnitude of $(i|(V_{core})_i|i)$ to be largest for oxygen and smallest for carbon. The fact that the sum of the first three terms of equation (88) does not exhibit this trend shows the importance of the fourth term in equation (88). This term is not included in Table 11, It will be treated when we discuss the effect of σ-π exchange.

Using the carbon atom as an example calculation, we compute the value of the kinetic energy of the p-electron as +1.230 au. The p-electron-nucleus-attraction term has a value of -4.704 au. The total, in column one, is -3.474 au. The π-electron, σ-core repulsion for carbon is computed from the equation

$$\sigma\text{-}\pi \text{ repulsion} = P^{LOAO}_{1s\ 1s}\ (\pi\ \pi|1s\ 1s) + P^{LOAO}_{2s\ 2s}\ (\pi\ \pi|2s\ 2s) + P^{LOAO}_{2p\sigma\ 2p\sigma}\ (\pi\ \pi|2p\sigma\ 2p\sigma).$$

We approximate the $P^{LOAO}_{\lambda\lambda}$ by atomic populations, with an s-p promotion of one electron, and obtain the electron repulsions to give

$$\sigma\text{-}\pi \text{ repulsion} = 2(0.775 \text{ au}) + 0.576 \text{ au} + 2(0.547 \text{ au}),$$

or

$$\sigma\text{-}\pi \text{ repulsion} = 3.220 \text{ au}.$$

The approximation of $P^{LOAO}_{\lambda\lambda}$ by the AO populations of isolated atoms can be improved upon. There are σ-core polarization effects in a molecule which change the electronic populations of the atoms. We shall, in a later section, introduce a method to approximately include this polarization effect.

The two-center terms, $(i|(V_{core})_j|i)$, are a sum of two parts, the π-electron, nucleus attractions and the π-electron, σ-core repulsions. We have calculated these terms for all possible pairs of the atoms carbon, nitrogen, oxygen, and hydrogen. The calculations were performed with the same approximations for $P_{\lambda\lambda}^{LOAO}$ used in the calculation of the terms $(i|(V_{core})_i|i)$. We have calculated the attractions and repulsions over several internuclear distances. Roothaan's formulas were used to calculate the electron-nucleus attractions, and the tables of Sahni and Cooley were used to obtain the electron-electron repulsions. The object of this exercise was to obtain an equation in R_{ij}, the internuclear distance of i and j, which would approximate the accurate calculations.

We shall illustrate the approximation techniques for the specific example of an oxygen π-electron interacting with the nucleus and σ-electrons of nitrogen. For the remainder of the interaction pairs, we list only the results.

A plot of the oxygen π-electron, nitrogen-nucleus attraction energy, $(\pi_O(1)| - V_N(1)|\pi_O(1))$, versus R_{NO} appears in figure 4. Table 12 shows the coordinates of the points on the graph. We have made similar plots of the integral $(\pi_i(1)| - V_j(1)|\pi_i(1))$, for all the other pairs of C, N, and O π-electrons and C, N, O, and H nuclei. In every case, the plots show a similar shape to that of figure 4.

We computed the values of the oxygen π-electron, nitrogen σ-core repulsion energies at each R_{NO} with the equation

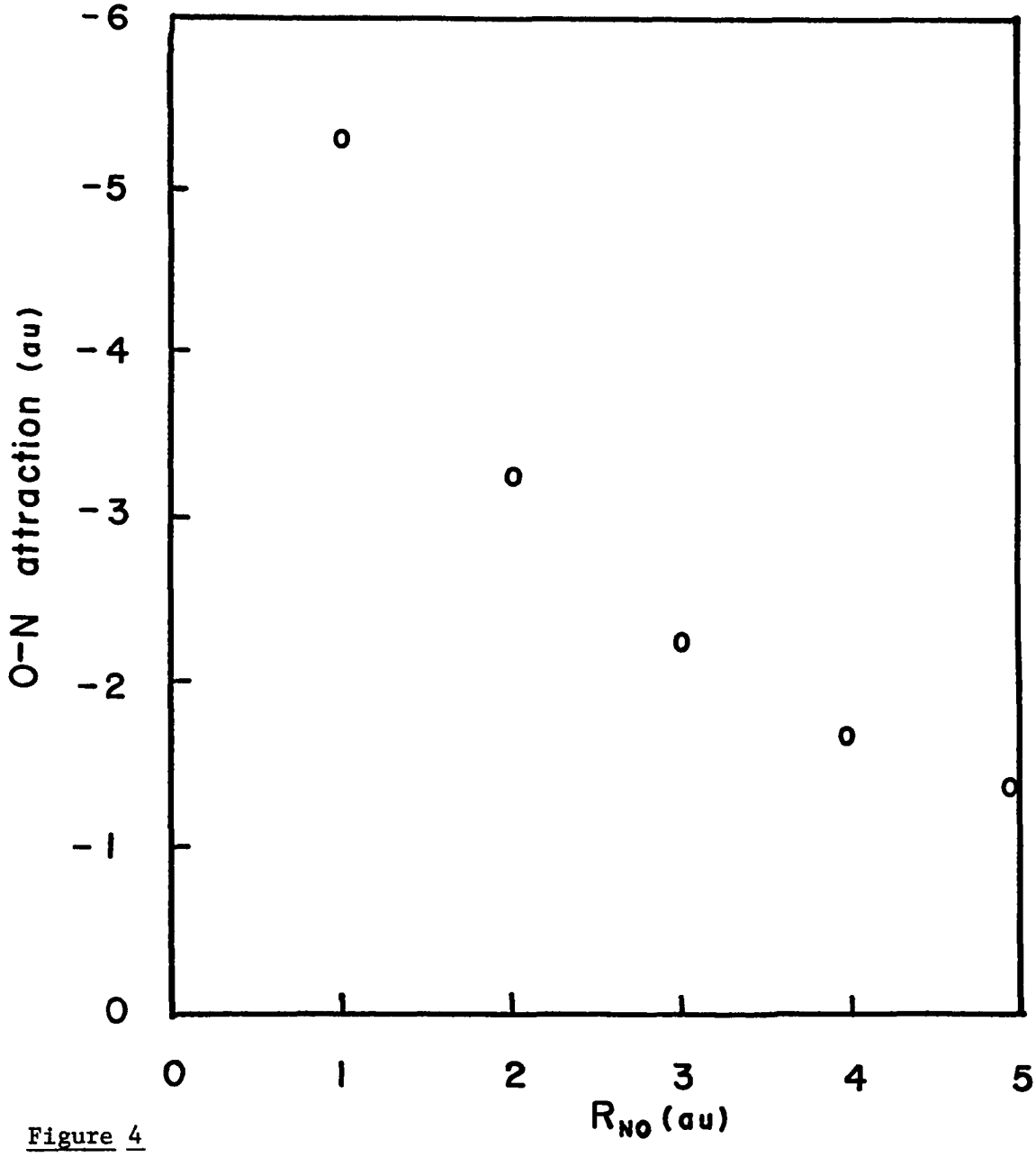


Figure 4

Oxygen π-electron, nitrogen nucleus attraction at one-au intervals in the internuclear distance R_{NO}.

Table 12

Oxygen π-Electron, Nitrogen Nucleus Attraction Energy, $(\pi_O(1)| - V_N(1)|\pi_O(1))$, for Several Internuclear Distances

R_{NO} (au)	$(\pi_O(1)\| - V_N(1)\|\pi_O(1))$ (au)
1.0	-5.271
2.0	-3.241
3.0	-2.254
4.0	-1.715
5.0	-1.379

$$\sum_{\lambda=\sigma} P^{LOAO}_{\lambda\lambda} (\pi_O\ \pi_O|\lambda\ \lambda) = P^{LOAO}_{1s_N\ 1s_N} (\pi_O\ \pi_O|1s_N\ 1s_N)$$

AO's on N

$$+ P^{LOAO}_{2s_N\ 2s_N} (\pi_O\ \pi_O|2s_N\ 2s_N) + P^{LOAO}_{\sigma_N\ \sigma_N} (\pi_O\ \pi_O|\sigma_N\ \sigma_N)$$

$$+ P^{LOAO}_{\pi_N'\ \pi_N'} (\pi_O\ \pi_O|\pi_N'\ \pi_N'),$$

where σ_N and π_N' are, respectively, the nitrogen p AO's pointing towards oxygen and pointing at a ninety degree angle to the oxygen-nitrogen line of centers. We assume that $P^{LOAO}_{\pi_N'\ \pi_N'} = P^{LOAO}_{\sigma_N\ \sigma_N} = 1$, that $P^{LOAO}_{1s_N\ 1s_N} = 2$, and that $P^{LOAO}_{2s_N\ 2s_N} = 2$. We obtained values for the AO-repulsion integrals from the tables of Sahni and Cooley. The results of these calculations are plotted versus R_{NO} in figure 5, and the data for the plot are in Table 13. Similar calculations were performed on the repulsion energy of all other pairs of π-electron, σ-core interactions. In each case, the shape of the plot was very similar to that of figure 5.

The shape of the plot in figure 4 is very similar to the shape of the plot in figure 5. It appears that it is possible to fit both curves by the same basic formula. In order to establish the form of this basic equation, we used the fact that, at large R_{ij}, both the nucleus-electron attractions and electron-electron repulsions are well approximated by a simple point-charge potential,

$$(i(1)|\ -V_j(1)|i(1)) \approx -Z_j/R_{ij} \qquad (90)$$

and

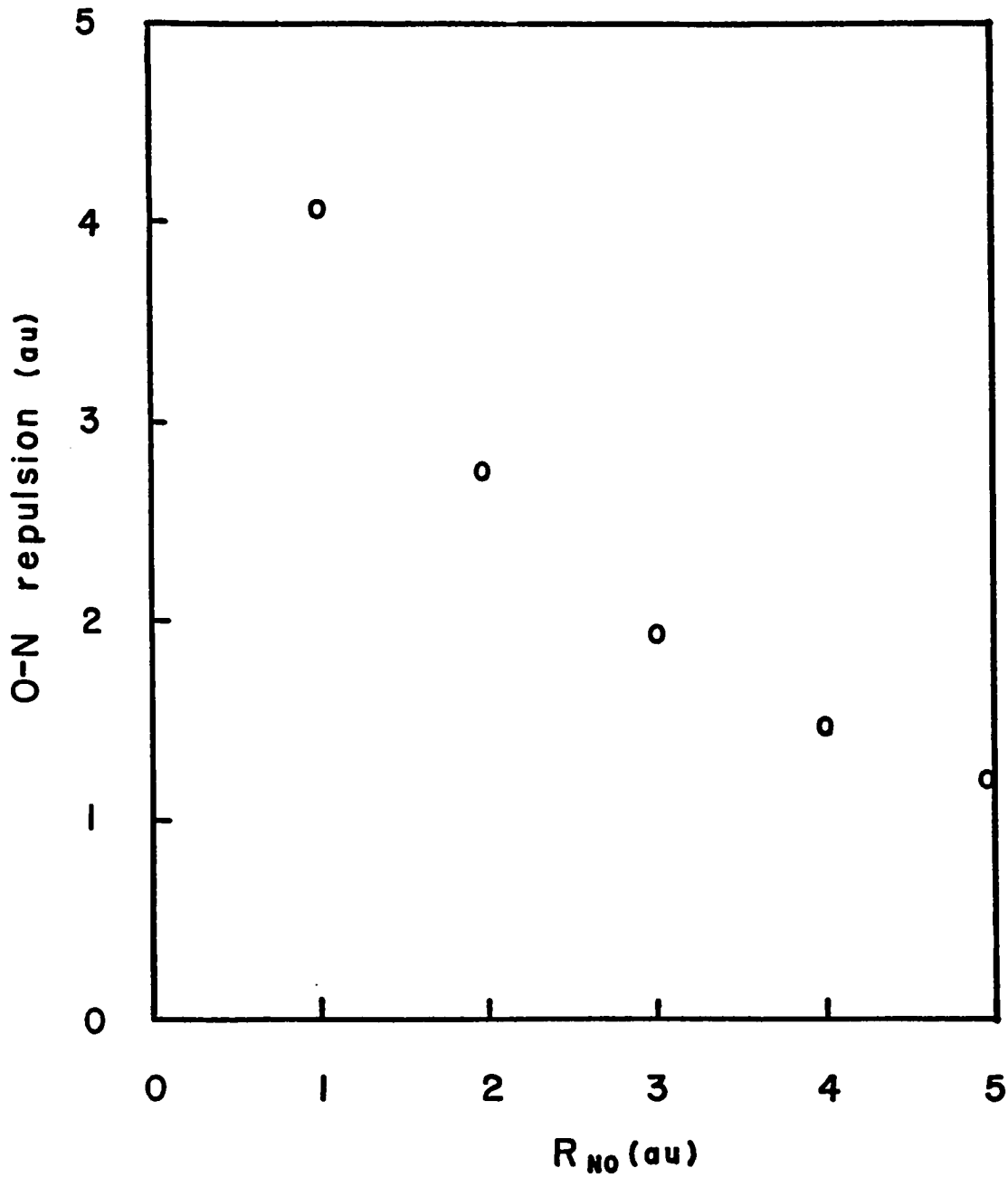


Figure 5

Oxygen π-electron, nitrogen σ-core repulsion at one-au intervals in the internuclear distance R_{NO}.

Table 13

Oxygen π-Electron, Nitrogen σ-Core Repulsion Energy for Several Internuclear Distances

R_{NO} (au)	π-Electron, σ-core repulsion (au)
1.0	4.059
2.0	2.740
3.0	1.941
4.0	1.473
5.0	1.189

$$\sum_{\substack{\lambda=\sigma \\ \text{AO's on } j}} P_{\lambda\lambda}^{\text{LOAO}} \, (i(1)\ i(1)|\lambda(2)\ \lambda(2)) \simeq N_j/R_{ij} \qquad (91)$$

(for R_{ij} large),

where Z_j is the charge on the j-nucleus and N_j is the number of electrons in the σ-core of j.

At smaller R_{ij}, the point-charge approximation overestimates the magnitudes of both terms. We should correct the point-charge approximation by including a term to decrease the results of this approximate treatment. Since the point-charge approximation is good at large R_{ij}, this term should go to zero as R_{ij} tends to infinity. A reasonable way to include such a term is shown in the equation

$$I_{ij} = (Q_j/R_{ij}) \{1 - (D_{ij}/R_{ij})\}, \qquad (92)$$

where i is the atom bearing the π-electron, I_{ij} is either a nucleus-electron attraction or an electron-electron repulsion, $Q_j = -Z_j$ if I_{ij} is a nucleus-electron attraction, and $Q_j = N_j$ if I_{ij} is an electron-electron repulsion. D_{ij} is a parameter which depends upon the nature of the i-j pair and on whether I_{ij} is an attraction or repulsion.

We determined, by trial and error, that D_{ij} could be represented in terms of three basic parameters A, B, and C, in the equation

$$D_{ij} = A + B/C^{R_{ij}}. \qquad (93)$$

The parameters A, B, and C depend upon the nature of the i-j pair and upon the nature of I_{ij}. We obtained A, B, and C values, which are of adequate accuracy, by solving equation (92) for D_{ij}, given I_{ij}, Q_j, and

R_{ij}. The results were then plotted versus R_{ij}. An example of such a plot, the D_{ON} for the oxygen π-electron, nitrogen σ-core interaction, is in figure 6. At large values of R_{ij}, D_{ij} assumes a fairly constant value. This value becomes the A-parameter. In order to find the B and C parameters, we need only to solve equation (93) at two values of R_{ij}. R_{ij} = 2.0 au and R_{ij} = 4.0 au bracket the usual bond lengths for molecules. Below 2.0 au, the equation for I_{ij} gives erratic results and should not be used.

The parameters which were arrived at by this technique are shown in Tables 14 and 15. Table 14 contains data for the nucleus-electron attractions, and Table 15 contains data for the repulsions. We calculated I_{ij} with equation (92) and the parameters of Tables 14 and 15 at R_{ij} = 3.0 au and R_{ij} = 5.0 au. Tables 16 and 17 compare the results of the approximate calculations to the results obtained from Roothaan's formulas or the Sahni and Cooley tables.

The approximate calculations give results which are within at least 0.3 electron volts of the results of the accurate calculations. These comparisons lead us to believe that the use of the approximate formulas will cause errors of no more than ± $\frac{1}{2}$ ev in experimentally obtainable quantities determined by accurate calculations. We therefore judge the values of the A, B, and C parameters to be of adequate accuracy.

One can simplify the approximate determination of $(i|(V_{core})_j|i)$ even further by combining the equations for the attractions and repulsions into one equation giving the interaction energy of an i π-electron with the total core of j. When this is done, one has an approximation to $(i|(V_{core})_j|i)$ in terms of a five-parameter function. We term this

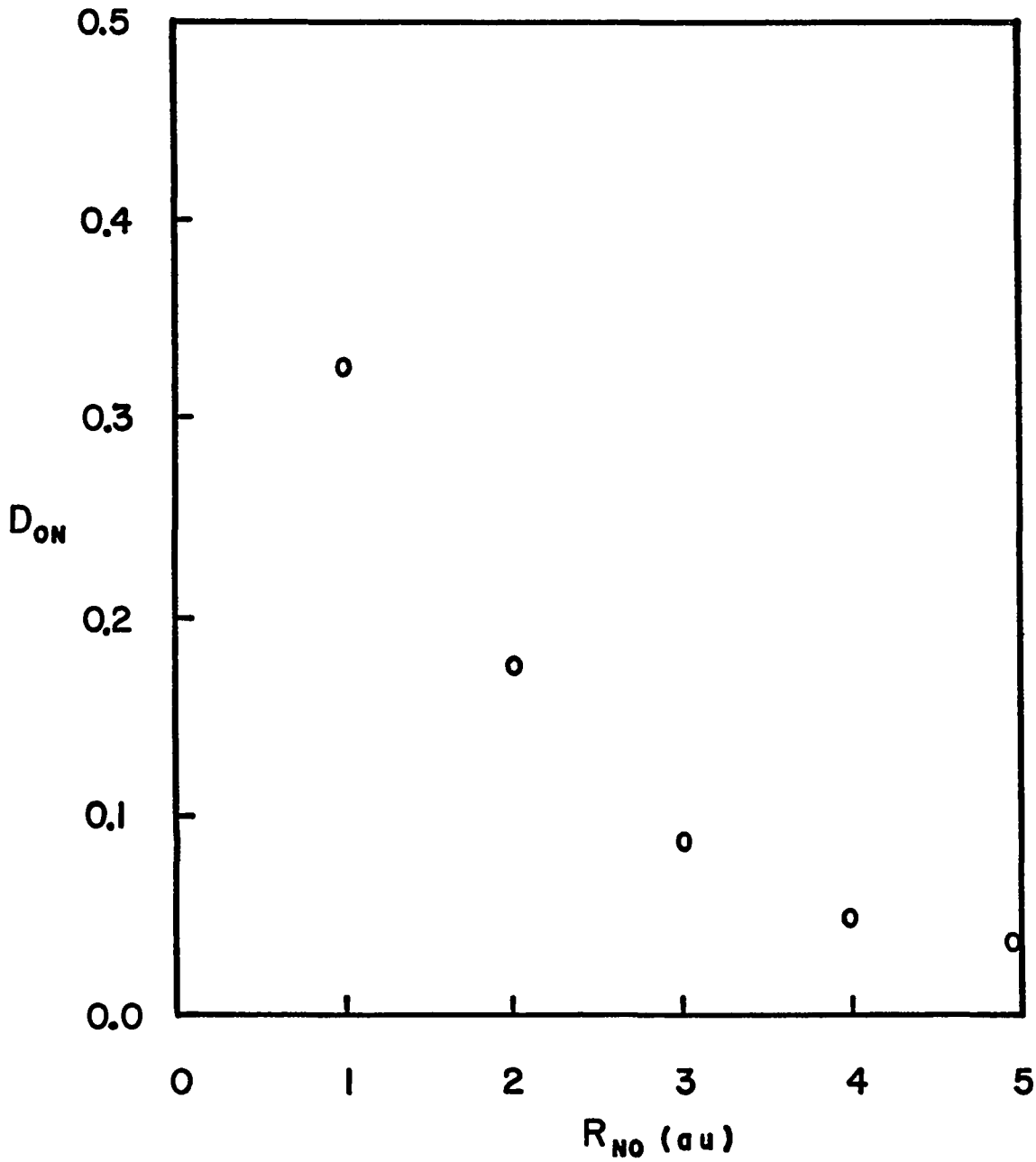


Figure 6

The parameter D_{ON}, in au, computed from the oxygen π-electron, nitrogen σ-core repulsion as a function of the internuclear distance R_{NO}.

Table 14

Parameters Needed in the Approximate Calculation of Two-Center π-Electron, Nucleus Attraction Integrals

Atom Bearing the π-electron	A	B	C
C	0.100	0.820	2.08
N	0.100	0.650	2.24
O	0.070	0.610	2.79

Table 15

Parameters Needed in the Calculation of Two-Center

π-Electron, σ-Core Repulsions

Atom Pair (The first atom bears the π-electron)	A	B	C
O, H	0.075	1.56	2.94
N, H	0.050	0.854	1.82
C, H	0.025	0.955	1.63
C, C	0.075	1.68	2.60
N, N	0.050	1.36	2.59
O, O	0.025	0.748	2.38
C, O	0.075	1.32	2.44
C, N	0.075	1.57	2.56
N, O	0.050	0.833	2.29
N, C	0.050	1.61	2.71
O, C	0.025	1.21	2.70
O, N	0.025	0.940	2.53

Table 16

Comparisons of Approximate Calculations of π-Electron, Nucleus Attraction Integrals to More Accurate Calculations

π-electron, nucleus pair	R (au)	Accurate[a] Value (au)	Approximate[a] Value (au)	Error (ev)[b]
C, C	3.0	1.866	1.872	+0.16
	5.0	1.170	1.170	
C, N	3.0	2.177	2.184	+0.19
	5.0	1.365	1.365	
C, O	3.0	2.488	2.496	+0.22
	5.0	1.560	1.560	
N, C	3.0	1.908	1.902	-0.16
	5.0	1.176	1.176	
N, N	3.0	2.226	2.219	-0.19
	5.0	1.372	1.372	
N, O	3.0	2.544	2.536	-0.22
	5.0	1.568	1.568	
O, C	3.0	1.932	1.932	
	5.0	1.182	1.182	
O, N	3.0	2.254	2.254	
	5.0	1.379	1.379	
O, O	3.0	2.576	2.576	
	5.0	1.576	1.576	
C, H	3.0	0.311	0.312	+0.03
	5.0	0.195	0.195	
N, H	3.0	0.318	0.317	-0.03
	5.0	0.196	0.196	
O, H	3.0	0.322	0.322	
	5.0	0.197	0.197	

a) All terms have negative sign.

b) A blank indicates no error to about two decimal places in ev.

Table 17

Comparisons of Approximate Calculations of π-Electron, σ-Core Repulsions to More Accurate Calculations

π-electron, σ-core pair	R (au)	Accurate Value (au)	Approximate Value (au)	Error (ev)[a]
C, C	3.0	1.558	1.570	+0.32
	5.0	0.980	0.980	
C, N	3.0	1.873	1.884	+0.30
	5.0	1.176	1.176	
C, O	3.0	2.196	2.205	+0.24
	5.0	1.369	1.372	+0.08
N, C	3.0	1.594	1.595	+0.03
	5.0	0.985	0.985	
N, N	3.0	1.911	1.914	+0.08
	5.0	1.181	1.182	+0.03
N, O	3.0	2.241	2.240	-0.03
	5.0	1.381	1.379	-0.05
O, C	3.0	1.621	1.620	-0.03
	5.0	0.989	0.990	+0.03
O, N	3.0	1.938	1.944	+0.16
	5.0	1.189	1.188	-0.03
O, O	3.0	2.264	2.268	+0.11
	5.0	1.386	1.393	+0.19
C, H	3.0	0.305	0.306	+0.03
	5.0	0.196	0.196	
N, H	3.0	0.313	0.313	
	5.0	0.197	0.196	-0.03
O, H	3.0	0.317	0.318	+0.03
	5.0	0.198	0.197	-0.03

a) A blank indicates no error to about two decimal places in ev.

approximation V_{ij}, with $(i|(V_{core})_j|i) \approx V_{ij}$, and write

$$V_{ij} = (1/R_{ij}) \{\rho_j + (1/R_{ij}) (A' + B'/(C')^{R_{ij}} - D/(E)^{R_{ij}})\}, \quad (94)$$

where

$$\rho_j = -1.00 \text{ if } j \text{ is an atom other than hydrogen}$$

and

$$\rho_j = 0.00 \text{ if } j \text{ is hydrogen.}$$

If one takes ρ_j to be -1.00 for atoms other than hydrogen, he assumes that the atom contributes only one electron to the π-system. If the atom contributes two electrons to the π-system, at the expense of the σ-electrons, then ρ_j should be -2.00. ρ_j is the negative of the charge on the σ-core. A', B', C', D, and E are the five parameters listed in Table 18.

With the exception of the final term in the equation for $(i|(V_{core})_i|i)$, we have approximated the π-electron, core interaction potentials. If one can take account of this term and calculate the π-π electron repulsions, he can use the previously developed approximations and equation (49) to calculate $F_{\mu\mu}^{LOAO}$.

(E) Approximate Equations for the π-π Repulsions

The one-center π-electron repulsions can be calculated from a knowledge of the orbital exponents defining the basis set of AO's (Table 8). We have determined these repulsions from the Sahni and Cooley integral tables, and the one-center π-π repulsions are

Table 18

Parameters Needed in the Calculation of the

π-Electron, Core Interaction Energy

π-electron, core atom pair	A'	B'	C'	D	E
C, H	0.075	0.820	2.08	0.955	1.63
C, C	0.225	4.92	2.08	8.40	2.60
C, N	0.250	5.74	2.08	9.42	2.56
C, O	0.275	6.56	2.08	9.24	2.44
N, H	0.050	0.650	2.24	0.854	1.82
N, C	0.350	3.90	2.24	8.05	2.71
N, N	0.400	4.55	2.24	8.16	2.59
N, O	0.450	5.20	2.24	5.83	2.29
O, H	-0.005	0.610	2.79	1.56	2.94
O, C	0.295	3.66	2.79	6.05	2.70
O, N	0.340	4.27	2.79	5.64	2.53
O, O	0.385	4.88	2.79	5.24	2.38

$$(\pi_C\ \pi_C \mid \pi_C\ \pi_C) = 0.613 \text{ au},$$

$$(\pi_N\ \pi_N \mid \pi_N\ \pi_N) = 0.750 \text{ au}, \tag{95}$$

and

$$(\pi_O\ \pi_O \mid \pi_O\ \pi_O) = 0.870 \text{ au}.$$

One could obtain the two-center π-electron repulsions by using Roothaan's equations. However, the success of the previously developed three-parameter approximate equation in reproducing the nucleus-electron attractions and π, σ-core repulsions led us to attempt to use this same technique for the two-center π-π repulsions. Again, at large R_{ij} the π-π repulsions can be approximated by a point-charge potential. At smaller R_{ij} the point-charge approximation over-estimates the value of the integral. We computed the two-center π-π repulsions and plotted them versus R_{ij}. Equations (92) and (93) were found to apply very well for the π-π repulsions. We therefore extended these equations to

$$\Pi_{ij} = (1/R_{ij})\ \{1 - (D_{ij}/R_{ij})\}, \tag{96}$$

where D_{ij} is defined as in equation (93), and Π_{ij} is an approximation to the repulsion of an electron in a π AO on atom i and an electron in a π AO on atom j. The A, B, and C parameters for Π_{ij}, established by the same techniques used earlier, are given in Table 19.

The π-π repulsions computed with the Π_{ij} agree very well with the actual values of the integrals. Tests of Π_{ij} versus accurate calculations of the integrals revealed no errors greater than 0.05 ev. This level of error is not only acceptable but excellent.

Table 19

Parameters Needed in the Calculation

of π-π Repulsions

Atom Pair	A	B	C
C, C	0.200	1.07	2.15
C, N	0.175	0.920	2.08
C, O	0.175	0.908	2.29
N, N	0.150	0.644	1.95
N, O	0.125	0.490	1.76
O, O	0.100	0.490	1.87

(F) Inclusion of σ-π Exchange Energy

The *ab initio* investigations of Cook, Hollis, and McWeeny and the semi-empirical calculations of Dewar and Baird have emphasized that a modification of the all-electron CNDO formalism is required. The neglect of one-center electron-repulsion integrals of the type (ij | ij), which is a part of CNDO theory, is unjustified. The retention of such integrals gives us a formalism similar to the NDDO formalism.[7] The NDDO formalism would, however, retain more electron repulsion integrals than the CNDO integrals and the (ij | ij) type.

Work done by Edmiston and Ruedenberg in developing a method for transforming MO's to localized orbitals by the minimum-exchange-energy principle provides some useful data on the exchange energy of σ and π MO's.[61] One can sum the σ-π MO exchange energies for a given π-MO in a molecule and obtain the total σ-π exchange energy for an electron of the π-MO. The results of such summations, for several diatomic molecules, are in Table 20. These energies are certainly not small or negligible. They are all on the order of six ev. Although Edmiston and Ruedenberg employ "best molecule AO's" in their calculations, they point out that the exchange energy is not very sensitive to AO-type.

One wonders what integrals are involved in the calculation of σ-π exchange energy, and how the integrals can be included in an approximate π-MO theory. We consider the carbon monoxide molecule as a specific example. For a basis set of orbitals (formally LOAO's), π_C, σ_C, $2s_C$ and π_O, σ_O, and $2s_O$, the exchange energy of an electron in one of CO's π-MO's and the σ-MO's of CO is as follows:

Table 20

σ, π-Electron Exchange Energies for

Some Diatomic Molecules

Molecule	σ-π exchange (au)
N_2	0.201
CO	0.217
F_2	0.254
LiF	0.237
BF	0.257

$$C_{\pi_C}^2 \{ \sum_i C_{\sigma_C i}^2 (\pi_C\ \sigma_C | \pi_C\ \sigma_C) + \sum_i C_{2s_C i}^2 (\pi_C\ 2s_C | \pi_C\ 2s_C)$$

$$+ 2 \sum_i C_{\sigma_C i}\, C_{2s_C i} (\pi_C\ \sigma_C | \pi_C\ 2s_C)\} + C_{\pi_O}^2 \{ \sum_i C_{\sigma_O i}^2 (\pi_O\ \sigma_O | \pi_O\ \sigma_O)$$

$$+ \sum_i C_{2s_O i}^2 (\pi_O\ 2s_O | \pi_O\ 2s_O) + 2 \sum_i C_{\sigma_O i}\, C_{2s_O i} (\pi_O\ \sigma_O | \pi_O\ 2s_O)\}$$

$$+ 2 C_{\pi_C}\, C_{\pi_O} \{ \sum_i C_{\sigma_C i}\, C_{\sigma_O i} (\pi_C\ \sigma_C | \pi_O\ \sigma_O) + \sum_i C_{\sigma_C i}\, C_{2s_O i} (\pi_C\ \sigma_C | \pi_O\ 2s_O)$$

$$+ \sum_i C_{2s_C i}\, C_{\sigma_O i} (\pi_C\ 2s_C | \pi_O\ \sigma_O) + \sum_i C_{2s_C i}\, C_{2s_O i} (\pi_C\ 2s_C | \pi_O\ 2s_O)\}. \quad (88)$$

The summations over i extend over occupied σ-MO's. The contribution to the σ-π exchange due to the 1s electrons may be estimated by adding the terms $C_{\pi_C}^2 (\pi_C\ 1s_C | \pi_C\ 1s_C)$ and $C_{\pi_O}^2 (\pi_O\ 1s_O | \pi_O\ 1s_O)$ to the above equation. Formally, the coefficients in the above equation are LOAO coefficients. In this equation, we have retained only those integrals which are retained in the NDDO formalism. It is a good approximation to calculate the electron-repulsion integrals in this equation over AO's rather than LOAO's.

The factor multiplied by $C_{\pi_C}^2$ in the CO exchange should be included in the carbon matrix element α_{CC}^{LOAO}, and the term multiplied times $C_{\pi_O}^2$ should be included in the oxygen matrix element α_{OO}^{LOAO}. The first two factors are specific examples of the integrals appearing in the last term of equation (88). The integrals $(\pi_C\ \sigma_C | \pi_C\ 2s_C)$ and $(\pi_O\ \sigma_O | \pi_O\ 2s_O)$ are identically zero. This means that these first two factors include the $(ij \mid ij)$ integrals necessary to improve CNDO. If the $(ij \mid ij)$ integrals are

included, one has partially accounted for the σ-π exchange energy. The multiplier of $2C_{\pi_O} C_{\pi_C}$, the C-O π bond-order, is the effect of σ-π exchange upon β_{CO}^{LOAO}.

We have calculated the exchange energy contribution to equation (88). The σ-AO populations were obtained from two sources, a calculation on CO molecule by Sahni,[62] and a calculation on H_2CO molecule by Goodfriend, Birss, and Duncan.[63] The σ-π exchange energy is mildly sensitive to the AO-populations used in its calculation. The H_2CO populations were used to calculate the σ-π exchange contributions for carbon and oxygen. These contributions should apply to C and O with σ-cores which are approximately sp^2 hybridized and are as follows:

$$\text{Carbon} = 0.128 \text{ au}$$

and

$$\text{Oxygen} = 0.262 \text{ au.}$$

We assumed the same σ-AO population for nitrogen as that used in earlier calculations for V_{ii} and V_{ij}. With this population, we obtained an exchange contribution for nitrogen of

$$\text{Nitrogen} = 0.215 \text{ au.}$$

All integrals were determined from the Sahni and Cooley tables with the AO's defined in Table 8.

The part of the σ-π exchange energy which goes into the off-diagonal matrix elements $F_{\mu\nu}^{LOAO}$ looks very much like it could be approximated by assuming that the σ-bonding MO's are formed from equally weighted hybrids. It is assumed that only the σ-MO which joins the μ and ν atoms provides a significant contribution to the σ-π exchange in the π matrix element

$F_{\mu\nu}^{LOAO}$. Lone pairs and σ-bonds with atoms other than μ and ν should contribute little to the σ-π exchange, as is witnessed by the small singlet-singlet and singlet-triplet splittings in n→π* transitions. Therefore, an estimate to the σ-π exchange effect on $\beta_{\mu\nu}^{LOAO}$ is $\frac{1}{2}$ $(\pi_\mu\ hy_\mu|\pi_\nu\ hy_\nu)$, where hy is a hybrid AO. For the CO molecule with sp hybrids, this term adds 0.027 au to F_{CO}^{LOAO}.

Assuming $C_{\pi_O}^2 = 0.60$, $C_{\pi_C}^2 = 0.40$, $2C_{\pi_C} C_{\pi_O} = 0.98$, 0.027 au for the multiplier of $2C_{\pi_C} C_{\pi_O}$, and the σ-AO populations of the Sahni wave function, one obtains about 0.21 au for the σ-π exchange energy of CO. This falls in the range of values calculated by Edmiston and Ruedenberg.

In Table 21 the contribution to $(i|(V_{core})_i|i)$ due to the last term of equation (88), the σ-π exchange term, is added to the results for the first three terms of this equation (Table 11). By way of analogy to V_{ij}, we call these approximate results for $(i|(V_{core})_i|i)$ the V_{ii}.

We label the effect of σ-π exchange upon β_{ij}^{LOAO}, $(EX)_{ij}$. $(EX)_{ij}$ is estimated by calculating the term $\frac{1}{2}$ $(\pi_i\ hy_i|\pi_j\ hy_j)$, where hy_i and hy_j are sp^2 hydrids located on atoms i and j respectively. These integrals are calculated for several values of R_{ij} and the results for all i-j pairs appear in Table 22.

Since all of the pairs produce about the same exchange contribution, an equation which fits the average of values for all pairs at each R_{ij} should be adequate. We employed the same three-parameter function used successfully for V_{ij} and Π_{ij}. The technique used to establish values for the parameters is the same as that employed earlier. The equation is

$$(EX)_{ij} = (1/2R_{ij}) \{1 - (- 30.18 + 30.06/(0.9693)^{R_{ij}}) / R_{ij}\}. \quad (97)$$

Table 21

One-Center π-Electron, Core Interaction Energies, V_{ii}

Atom i	Total from Table 11 (au)	σ-π exchange $(EX)_{ii}$ (au)	V_{ii} (au)
C	-0.254	-0.128	-0.382
N	-0.227	-0.215	-0.442
O	-0.257	-0.262	-0.519

Table 22

The Effect of σ-π Exchange Upon β_{ij}^{LOAO} ($(EX)_{ij}$)

i, j	$(EX)_{ij}$ (au)				
R_{ij} (au) =	1.0	2.0	3.0	4.0	5.0
C, O	0.035	0.025	0.010	0.005	0.002
C, C	0.030	0.025	0.013	0.006	0.003
N, N	0.038	0.024	0.010	0.004	0.002
O, O	0.043	0.021	0.007	0.003	0.001
N, O	0.040	0.023	0.008	0.003	0.002
N, C	0.033	0.025	0.011	0.005	0.002

This correction is added to β_{ij}^{LOAO} and puts the σ-π exchange into the off-diagonal Roothaan matrix elements of π LOAO's.

Now that we have completed the approximation of the σ-π exchange energy we have ready the main mathematical apparatus of our π-electron theory. This theory might be described as an *ab initio* ZDO theory plus σ-π exchange. It is an excellent approximation to the more general NDDO formalism. We would, however, like to make the theory a bit more flexible.

(G) Inclusion of σ-Core Polarization

One assumes that each atom i in a molecule either gains or loses a small fraction of its σ-electron population by way of core polarization. One can set Y(i) equal to the difference in σ-electronic charge of the atom i in the molecule and in the neutral atom. If i gains electrons by polarization effects, Y(i) is positive, and, if i loses electrons, Y(i) is negative. If i neither gains nor loses then Y(i) = 0. We need to reconsider any of the approximations we have developed which involve π-electron, σ-core interactions. These approximations are the V_{ij} and $(EX)_{ij}$. The $(EX)_{ij}$ terms are small and relatively insensitive to changes in the σ-electronic populations.

We wish to include the Y(j) in V_{ij} without complicating our previously developed formulas too much. Therefore, Y(j) is included in the two-center V_{ij} in an approximate way, giving reasonably accurate calculated results only where Y(j) is small in magnitude, say less than 0.1. Y(j) is included as a point-charge interaction. It interacts with the $i^{\underline{th}}$ π-electron by the potential $Y(j)/R_{ij}$.

For the diagonal V_{ij} terms, we average all the π, σ-core repulsions, obtaining the average σ-core repulsion per σ-electron. We assume that, when a small amount of σ-electronic charge is added to i or removed from i via polarization effects, this charge interacts with a π-electron on i through this average repulsion. This is not correct, but if Y(i) is small it should not cause much error. The V_{ii} terms of Table 21 are, therefore, redefined, without a change in notation, to the following:

$$\begin{aligned} V_{OO} &= -0.519 + 0.844\ Y(O), \\ V_{NN} &= -0.442 + 0.738\ Y(N), \\ &\text{and} \\ V_{CC} &= -0.382 + 0.618\ Y(C). \end{aligned} \tag{98}$$

One can include the Y(j) in the two-center V_{ij} by modifying the three-parameter approximate equation for the π-electron, σ-core repulsion to include the Y(j) as a point-charge interaction of Y(j) with the $i^{\underline{th}}$ π-electron. This three-parameter function can then be resynthesized with the function which approximates the nucleus-electron attractions to give a modified form of equation (94) for V_{ij}. We write this modified equation, without a change in notation, as

$$V_{ij} = (1/R_{ij})\ \{\rho_j + Y(j) + (1/R_{ij})\ (A' + B'/(C')^{R_{ij}} - D/(E)^{R_{ij}})\}. \tag{99}$$

The parameters A', B', C', D, and E are listed in Table 18.

These equations for V_{ii} and V_{ij} are the general equations for calculating π-core interactions in the case where σ-electronic charge is transferred from one atom to another. When Y(i) and Y(j) are zero, we obtain the previous equations for no σ-charge shifts. The Y(i) are parameters

which must be guessed. Some π-electron calculations should be insensitive to the values of Y(i), i.e. electronic transition energies. In the cases where the results of the π-electron calculations are dependent upon the Y(i), the Y(i) will have to be chosen by analogy to accurate σ-orbital calculations on smaller molecules.

(H) Summary

To summarize the derivation of the method, it is best to write the first approximations to the equations for the Roothaan SCF matrix elements, equations (49) and (50), in terms of the further approximations we have developed for the α^{LOAO}'s, β^{LOAO}'s, and π-π repulsions. Originally we had

$$F_{\mu\mu}^{LOAO} = \alpha_{\mu}^{LOAO} + \sum_{\sigma}^{\substack{MO's \\ occ.\ \pi}} P_{\sigma\sigma}^{LOAO} (\mu\mu|\sigma\sigma) - \frac{1}{2} P_{\mu\mu}^{LOAO} (\mu\mu|\mu\mu) \tag{49}$$

and

$$F_{\mu\nu}^{LOAO} = \beta_{\mu\nu}^{LOAO} - \frac{1}{2} P_{\mu\nu}^{LOAO} (\mu\mu|\nu\nu). \tag{50}$$

The π-π repulsions $(ii \mid jj)$ are approximated by Π_{ij}. With this approximation, equations (49) and (50) become

$$F_{\mu\mu}^{LOAO} = \alpha_{\mu}^{LOAO} + \sum_{\sigma}^{\substack{MO's \\ occ.\ \pi}} P_{\sigma\sigma}^{LOAO} \Pi_{\mu\sigma} - \frac{1}{2} P_{\mu\mu}^{LOAO} \Pi_{\mu\mu} \tag{100}$$

and

$$F_{\mu\nu}^{LOAO} = \beta_{\mu\nu}^{LOAO} - \frac{1}{2} P_{\mu\nu}^{LOAO} \Pi_{\mu\nu}. \tag{101}$$

One calculates the elements of the matrix (Π_{ij}) from equations (95) and

(96). The parameters required for calculations with equation (96) are found in Table 19.

The α_μ^{LOAO} are explicit functions of the $(\mu|(V_{core})_n|\mu)$, the $K_{\mu n}$, and the $S_{\mu n}$, and this dependence is shown in the previously derived equation, equation (83),

$$\alpha_\mu^{LOAO} = \Big(\prod_{n\neq\mu} B_{\mu n}\Big)^{-2} \Big[\Big\{\Big(\prod_{n\neq\mu} E_{\mu n}^2\Big) - \sum_{n\neq\mu}\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2/2\Big\}(\mu|(V_{core})_{local}|\mu) + \sum_{n\neq\mu}\Big\{\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2\{(1/2E_{\mu n}^2) - 1\}/2\Big\}(n|(V_{core})_{local}|n) - \sum_{n\neq\mu}\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2 K_{\mu n}\Big] + \Big(\mu\Big|\sum_{\substack{m\neq\mu \\ m\neq \text{ nearest } \pi\text{-bearing} \\ \text{neighbors-to-}\mu}} (V_{core})_m\Big|\mu\Big). \tag{83}$$

We have approximated the $(\mu|(V_{core})_n|\mu)$ by $V_{\mu n}$. The terms $(\mu|(V_{core})_{local}|\mu)$ are a sum of π-electron, σ-core interactions for the μ-core and the cores of the π-bearing nearest neighbors-to-μ. We write, therefore, the approximate relations

$$(\mu|(V_{core})_{local}|\mu) = (V_\mu)_{local} \tilde{=} \sum_{\substack{n=\mu \\ \text{and } \pi\text{-bearing nearest} \\ \text{neighbors-to-}\mu}} V_{\mu n}. \tag{102}$$

The last term in equation (83), the $\Big(\mu\Big|\sum_{\substack{m\neq\mu \\ m\neq \text{ nearest } \pi\text{-bearing} \\ \text{neightors-to-}\mu}} (V_{core})_m\Big|\mu\Big)$ term, we approximate by the relation

$$(\mu|\ \sum_{\substack{m\neq\mu \\ m\neq \text{nearest } \pi\text{-bearing} \\ \text{neighbors-to-}\mu}} (V_{core})_m|\mu) = (V_\mu)_{remote} \tilde{=} \sum_{\substack{m\neq\mu \\ m\neq \text{nearest } \pi\text{-bearing} \\ \text{neighbors-to-}\mu}} V_{\mu m}. \qquad (103)$$

We may now rewrite equation (83), including these approximations, to obtain

$$\alpha_\mu^{LOAO} = \Big(\prod_{n\neq\mu} B_{\mu n}\Big)^{-2} \Big[\Big\{\Big(\prod_{n\neq\mu} E_{\mu n}^2\Big) - \sum_{n\neq\mu}\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2/2\Big\} (V_\mu)_{local}$$

$$+ \sum_{n\neq\mu}\Big\{\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2 \{1/2E_{\mu n}^2) - 1\} / 2\Big\} (V_n)_{local}$$

$$- \sum_{n\neq\mu}\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2 K_{\mu n}\Big] + (V_\mu)_{remote}, \qquad (104)$$

where one should remember that all products Π and summations Σ which appear explicitly in this equation are taken over nearest neighbors-to-μ only. α_μ^{LOAO} is a function of elements of the matrix $(S_{\mu n})$, some elements of the matrix (V_{ij}), and of the parameters $K_{\mu n}$. Elements of $(S_{\mu n})$ may be calculated using Roothaan's formulas or estimated from Mulliken's tables. The elements of (V_{ij}) are defined by equations (98) and (99), and the parameters needed in equation (99) are listed in Table 18. The parameters $K_{\mu n}$ can be found in Table 9.

Our approximate equation for $F_{\mu\mu}^{LOAO}$, therefore, becomes

$$F_{\mu\mu}^{LOAO} = \alpha_\mu^{LOAO}\{(S_{\mu n}), (V_{ij}), (K_{\mu n})\} + \sum_{\sigma}^{\substack{occ.\ \pi \\ MO's}} P_{\sigma\sigma}^{LOAO}\, \Pi_{\mu\sigma} - \frac{1}{2} P_{\mu\mu}^{LOAO}\, \Pi_{\mu\mu}, \qquad (105)$$

where α_μ^{LOAO} is written as having explicit dependence upon elements of the matrices $\underset{\sim}{S}$, $\underset{\sim}{V}$, and $\underset{\sim}{K}$. One should use this equation as the means to

approximately calculate $F_{\mu\mu}^{LOAO}$.

We calculate the $\beta_{\mu\nu}^{LOAO}$ term from equation (68) and the exchange term $(EX)_{\mu\nu}$. We write $\beta_{\mu\nu}^{LOAO}$, without a notation change, as

$$\beta_{\mu\nu}^{LOAO} = S_{\mu\nu}(B_{\mu\nu}^2 \prod_{n\neq\mu,\nu} B_{\mu n} \prod_{m\neq\mu,\nu} B_{\nu m})^{-1} [\{ \prod_{m\neq\mu,\nu} E_{\mu m} \prod_{n\neq\mu,\nu} E_{\nu n}\} K_{\mu\nu} - \sum_{m\neq\mu,\nu} (S_{\mu m} + S_{\nu m}) / 4] + (EX)_{\mu\nu}, \quad (106)$$

where $(EX)_{\mu\nu}$ corrects equation (68) for the exchange of π with σ LOAO's. One can, therefore, write for the Roothaan matrix element $F_{\mu\nu}^{LOAO}$ the approximate equation

$$F_{\mu\nu}^{LOAO} = \beta_{\mu\nu}^{LOAO} \{(S_{\mu n}), K_{\mu\nu}, (EX)_{\mu\nu}\} - \frac{1}{2} P_{\mu\nu}^{LOAO} \Pi_{\mu\nu}. \quad (107)$$

Here we indicate the explicit functional dependence of $\beta_{\mu\nu}^{LOAO}$ upon some elements of the $\underset{\sim}{S}$ matrix, upon $K_{\mu\nu}$, and upon $(EX)_{\mu\nu}$. One should use this equation to approximately calculate $F_{\mu\nu}^{LOAO}$.

In actual calculations on the π-systems of molecules, we have found that the V_{ij} are in slight error at large R_{ij}. If an atom i has a large number of neighbors j beyond an R_{ij} of about 4.0 au these errors in V_{ij} accumulate to the extent of causing moderate errors in calculated ionization potentials. It is better, for R_{ij} = 4.0 au, or greater, to calculate V_{ij} by a simple point-charge approximation, that is, to take V_{ij} to be the negative of the core charge of j divided by R_{ij}. This amounts to leaving out the part of equation (99) for V_{ij} which depends upon A', B', C', D, and E for $R_{ij} \geq 4.0$ au.

In this work, we have derived an approximate *ab initio* π-electron

SCF MO theory. The basis set of functions used to expand the π-MO's is a set of approximate Löwdin orthogonalized atomic orbitals (LOAO's). These basis functions are employed to derive approximate equations for the matrix elements α_{μ}^{LOAO} and $\beta_{\mu\nu}^{LOAO}$, which are analagous to the parameterized one-electron integrals of semi-empirical theories. The LOAO populations, which may be calculated from the LOAO-coefficients resulting from the SCF calculations, should be good approximations to the populations which would have been obtained by Mulliken population analysis of calculations using a basis set of overlapping atomic orbitals (AO's).

The α_{μ}^{LOAO} and $\beta_{\mu\nu}^{LOAO}$ contain the effects of overlap-coupling in the molecule. These overlap effects couple the corresponding μ and μν AO matrix elements to their nearest neighbors. $\beta_{\mu\nu}^{LOAO}$ is the sum of a part containing these overlap-coupling effects and a part containing a contribution due to σ-π exchange. The first part of $\beta_{\mu\nu}^{LOAO}$, which includes the overlap-coupling, is analagous to the β's of semi-empirical theory. This term is a product of the overlap $S_{\mu\nu}$ and a term which contains the environmental effects due to nearest neighbors. For a simple, two π-AO molecule, the assumption that β is equal to a constant times S, an assumption which is employed in some of the semi-empirical theories, is found to be correct only in the case of small overlap. The overlap-coupling found in α_{μ}^{LOAO} has never been discussed in detail in any of the semi-empirical treatments. This coupling is vaguely hinted at in the development of CNDO/2.[9]

Our *ab initio* theory also includes simplification of the theoretical calculation of π-π repulsions and π, σ-core interactions. These interactions are determined by use of approximate equations much simpler than

the equations of Roothaan. The approximate equations are based upon a simple modified point-charge approximation to the integrals. The equations are not useful below an R_{ij} of about 2.0 au, but, for calculations on most molecules, this is no inconvenience.

We have tested the individual approximations by comparing the results of the approximate calculation to more accurate results wherever possible. The ultimate test of the method, however, lies in utilizing the entire apparatus of the theory in doing calculations on molecules. Calculations have been performed on the π-systems of a series of molecules, and the results of these calculations are presented and discussed in the next chapter.

CHAPTER V

CALCULATIONS WITH THE SCF METHOD

In the previous chapter, the equations necessary to construct an approximate, no-overlap, π-electron molecular orbital theory were derived. No semi-empirical techniques or parameterization were used in order to fit experimental data. The atomic basis for the derivations was a minimal set of Löwdin orthogonalized atomic orbitals (LOAO's), with the π-LOAO's being given in an approximate closed-form. The equations for the one-electron π-integrals in this basis explicitly showed the effects of overlap-coupling of the nearest-neighbor atoms in a molecule. The two-electron integrals were either computed directly from "best atom" atomic orbitals or approximated by formulas designed to reproduce the two-electron integrals calculated with "best atom" AO's.

In this chapter, the results of calculations using the full apparatus of the theory are shown for the π-systems of several molecules. The π-electron densities predicted by the theory are compared to the π-densities calculated by other theories, both theoretical and semi-empirical. The changes in the π-electron densities with σ-electronic charge shift from one atom to another are also examined. The ionization potentials predicted by this theory from Koopmans' theorem are compared to experimental ionization potentials. The deviations of the theoretical results from the experimental ionization potentials are discussed and suggestions are made as to how to bring the theoretical ionization potentials into better agreement with the experimental values. The theoretical ionization potentials are found to be dependent upon the assumed charge

shifts of the σ-core. For some molecules where experimental data is available, the π-π^* electronic transitions predicted by the theory are compared to experimental results. A method is suggested to correlate the theoretical molecular orbital results with the experimental values.

Finally, the π wave functions of molecules show greater changes with σ-charge shifts than do the total π-electron densities. This is demonstrated for the glyoxal molecule, where the expansion coefficients for the calculated molecular orbitals are shown for several σ-charge distributions.

In the molecular calculations which follow, experimental bond lengths and bond angles were used where possible. Experimental bond lengths and angles were used for formaldehyde,[63] ethylene,[64] glyoxal,[48] benzene,[65] pyridine,[66] 1,3-diazine,[67] 1,4-diazine,[68] butadiene,[69] and p-benzoquinone.[70] Acrolein was constructed from the bond lengths and angles of glyoxal and butadiene. For hexatriene, the bond lengths and angles were assumed to be the same as for butadiene.

(A) π-Electron Densities

The π-MO's are given as expansions in LOAO's by the equation

$$\bar{\Phi}_i = \sum_\mu C_{\mu i}^{LOAO} \phi_\mu . \tag{108}$$

The population of a π-LOAO ϕ_μ in a doubly occupied MO is given by $2(C_{\mu i}^{LOAO})^2$, and the electronic population of the ϕ_μ LOAO in the molecule is the sum of the ϕ_μ populations for each MO (the $\mu^{\underline{th}}$ diagonal element of the bond-order matrix),

$$P_{\mu\mu}^{LOAO} = \sum_{i}^{\substack{occ.\ \pi \\ MO's}} 2(C_{\mu i}^{LOAO})^2. \tag{109}$$

We can expect that the π-LOAO populations are good approximations to the π-AO populations given by Mulliken population analysis.[43] Therefore, we have $P_{\mu\mu}^{LOAO} \simeq P_{\mu\mu}^{AO}$, and we drop the LOAO superscript from the population and index the population by a single subscript,

$$P_{\mu} = \sum_{i}^{\substack{occ.\ \pi \\ MO's}} 2(C_{i\mu}^{LOAO})^2. \tag{110}$$

Regardless of whether LOAO population analysis or Mulliken population analysis is used, we should obtain the same atomic populations for π atomic orbitals.

A close examination of the π-densities of several molecules should show the accuracy of the present theory in predicting these densities. The molecules are formaldehyde, butadiene, hexatriene, pyridine, glyoxal, and acrolein. The total π-electron densities are shown for these molecules in Table 23. We list, for each molecule, several sets of Y-parameters and the π-densities for each set of Y's. One should note particularly the changes in π-densities which occur when the σ-charges are changed. One should also note that, unlike Pariser-Parr-Pople theory, hydrogens are explicitly included in the present theory. The presence of the hydrogens influences the π-densities to a surprising extent.

The formaldehyde molecule is especially interesting. If no σ-charge shift is assumed, i.e. {Y} = {0}, then the π-MO shows oxygen

Table 23

π Charge Densities for Several Sets of the Core Polarization Parameters Y(i).[a]

1) Formaldehyde (H_2CO)

Set	Y(C)	Y(O)	Y(H)	P_C	P_O
(1)	0.00	0.00	0.00	0.95	1.05
(2)	0.02	0.04	-0.03	0.99	1.01
(3)	0.03	0.06	-0.045	1.02	0.98
(4)	0.04	0.08	-0.06	1.04	0.96

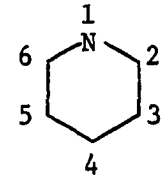
2) Butadiene (C=C-C=C)
1 2 3 4

Set	Y(C-1)	Y(C-2)	Y(H)	P_{C-1}	P_{C-2}
(1)	0.04	0.02	-0.02	1.05	0.95
(2)	0.08	0.04	-0.04	1.06	0.94

3) Hexatriene (C=C-C=C-C=C)
1 2 3 4 5 6

Set	Y(C-1)	Y(C-2)	Y(C-3)	Y(H)	P_{C-1}	P_{C-2}	P_{C-3}
(1)	0.00	0.00	0.00	0.00	1.05	0.96	0.99
(2)	0.04	0.02	0.02	-0.02	1.05	0.96	0.99
(3)	0.08	0.04	0.04	-0.04	1.06	0.95	0.99

4) Pyridine



Set	Y(N)	Y(C-2)	Y(C-3)	Y(H)	P_N	P_{C-2}	P_{C-3}	P_{C-4}
(1)	0.00	0.00	0.00	0.00	0.96	1.02	1.00	1.01
(2)	0.04	0.00	0.02	-0.02	0.94	1.03	1.00	1.01
(3)	0.03	0.015	0.03	-0.03	0.94	1.03	1.00	1.01
(4)	0.02	0.03	0.04	-0.04	0.95	1.03	1.00	1.01

5) Glyoxal (O=C-C=O)

Set	Y(O)	Y(C)	Y(H)	P_O	P_C
(1)	0.00	0.00	0.00	1.07	0.93
(2)	0.02	0.01	-0.03	1.06	0.94
(3)	0.04	0.01	-0.05	1.04	0.96
(4)	0.04	-0.01	-0.03	1.04	0.96

6) Acrolein (O=C-C=C)

1 2 3 4

Set	Y(O)	Y(C-2)	Y(C-3)	Y(C-4)	Y(H)	P_O	P_{C-2}	P_{C-3}	P_{C-4}
(1)	0.00	0.00	0.00	0.00	0.00	1.07	0.92	0.96	1.04
(2)	0.02	0.00	0.02	0.04	-0.02	1.06	0.94	0.96	1.05
(3)	0.02	0.02	0.04	0.08	-0.04	1.06	0.94	0.95	1.05

a) These results are obtained by SCF-iteration to a self consistency of 0.01 in the bond order matrix.

polarity. As we allow σ-electronic charge to shift from the hydrogens to carbon and from carbon to oxygen, the oxygen polarity of the π-MO diminishes. Finally, the polarity of the π-MO changes and becomes polar in the carbon direction.

The non-classical carbon polarity of the occupied π-MO of formaldehyde has been shown by other theoretical calculations which include all electrons. The calculations of Goodfriend, Birss, and Duncan[63] and of Cook and McWeeny[37] show this behavior. The first calculation obtained $P_C = 1.04$ and $P_O = 0.96$, while Cook and McWeeny calculated $P_C = 1.03$ and $P_O = 0.98$.

One could obtain sets of Y-parameters from the σ-MO populations of these theoretical calculations. Population analysis of the wave function of Goodfriend, Birss, and Duncan and comparison of the σ-atomic populations to the populations of neutral atoms produce the Y-set, Y(H) = -0.10, Y(C) = 0.06, and Y(O) = 0.14. Qualitatively, this Y-set resembles the Y-sets which give carbon polarity with the present method. However, the parameters of this set are all larger. One might expect such a discrepancy. Our method of including the Y's for two-center interactions and one-center interactions overestimates the effects of the charge shifts. This is so because the effect of Y upon the two-center repulsions is represented as a point-charge, and the effect of Y upon the one-center repulsions is through an average of all σ-AO repulsions. The Y-set deduced from the calculations of Cook and McWeeny is Y(H) = -0.06, Y(C) = 0.08, and Y(O) = 0.04. These Y's are unlike the Y-values from Table 23 necessary to reproduce the π-densities of Cook and McWeeny. These Y's also disagree with the Y-values determined from the σ-densities of

Goodfriend, Birss, and Duncan. It is only fair to mention that Newton and Palke[71] redid the work of Goodfriend, Birss, and Duncan and obtained a moderately different wave function. Their π-densities look to be almost identical.

From the previous discussion concerning the formaldehyde molecule, we may conclude that the present method predicts the proper π-electron densities for formaldehyde if we assume a Y-set based mainly upon classical ideas of electronegativity. Trying to pick a Y-set from the results of theoretical all-electron calculations appears to be a very frustrating procedure.

On the other hand, the CNDO semi-empirical theory shows the incorrect oxygen polarity for the π-MO of formaldehyde. The CNDO/1 calculation of Pople, Santry, and Segal[8] gives $P_C = 0.98$ and $P_O = 1.02$. The CNDO/2 calculation of Cook and McWeeny gives $P_C = 0.85$ and $P_O = 1.15$.

The π-densities of butadiene and hexatriene show that the larger the number of hydrogens a carbon has, the greater that carbon's π-electron density. It is assumed in the calculations that no σ-charge shift occurs between carbons, the only σ-shift occuring between carbon and hydrogen. This behavior of the π-densities is not shown in Pariser-Parr-Pople π-electron theory where the hydrogens are neutral, non-interacting parts of the core.

The effect of the hydrogens is not small. It appears from Table 23 that a pair of H's on a carbon increase the carbon's matrix element to about that for oxygen. Compare the π-densities of butadiene, glyoxal, and acrolein. This is also shown by the almost non-polar π-orbital of formaldehyde, where a carbon with two H's competes with oxygen for π-density.

Pyridine's π-densities disagree somewhat with what one would intuitively expect. With any choice of Y-set in Table 23, P_N is always less than 1.00. All P_C are 1.00 or greater. Classically, one would expect the more electronegative nitrogen to have more of the π-density than carbon. The work of Del Bene and Jaffé[11] in producing a CNDO/2 for spectra gives the following π-densities for pyridine: $P_N = 1.16$, $P_{C-2} = 0.91$, $P_{C-3} = 1.04$, and $P_{C-4} = 0.93$ (same atomic labels as in Table 23). These authors compare the electron densities produced by their method to those calculated by Clementi[1] from a Gaussian orbital basis. His results for pyridine are as follows: $P_N = 1.01$, $P_{C-2} = 1.00$, $P_{C-3} = 1.00$, and $P_{C-4} = 0.97$. These densities are actually closer to the π-densities calculated with the present π-electron theory than they are to the all-electron, semi-empirical calculations of Del Bene and Jaffé. For pyridine, the π-densities don't seem to be too sensitive to the σ-charge shifts in the core.

The results for the molecules glyoxal and acrolein are interesting when they are compared to butadiene. All three molecules show about the same π-electron densities. It appears, from the acrolein example, that, in competition for π-electronic charge, an oxygen atom competes against a carbon atom having one H slightly better than a carbon with two H's competes against a carbon atom with only one H. The oxygen atom at one end of acrolein has slightly greater π-density than the carbon at the other end. In acrolein and glyoxal, one does not find the shift in π-density from oxygen to carbon that one finds in formaldehyde. The reason for this is now clear. In acrolein and glyoxal, the oxygen competes for π-charge against a carbon with only one bonded hydrogen, not two.

(B) π Ionization Potentials

By Koopmans' theorem, we can obtain approximations to the vertical ionization potentials of molecules by taking the negative of the orbital energies. We apply this theorem to the first π ionization potentials of several molecules. The ionization potentials calculated for each Y-set of the molecules are shown in Table 24. It appears that the ionization potentials vary about one-half electron volt over the range of Y-values shown in the table. Therefore, if we compare ionization potentials for a series of molecules, we need to pick comparable Y-sets for the series.

In Table 25, we show calculated vertical ionization potentials (Koopmans' theorem), experimental ionization potentials, and the errors in the calculated results. The Y-set used to obtain the calculated ionization potential for each molecule is given in parentheses.

All the experimental ionization potentials are vertical except those of p-benzoquinone and hexatriene. These ionization potentials were determined respectively by photoelectron spectroscopic and Rydberg series methods and are adiabatic rather than vertical. The vertical ionization potentials are usually from 0.1 to 0.5 electron volts greater than the adiabatic ionization potentials.

The first ionization potentials of pyridine, 1,3-diazine, and 1,4-diazine are interpreted to be π ionization potentials rather than ionization potentials of electrons in non-bonding MO's on nitrogen. This interpretation is justified by the results of Al-Joboury and Turner[72] for the first adiabatic ionization potential of pyridine. This ionization

Table 24

π Ionization Potentials for Several Sets of the Core Polarization Parameters Y(i)[a]

1) Ethylene

Set	Y(C)	Y(H)	First π I.P. (ev)
(1)	0.00	0.00	9.8
(2)	0.04	-0.02	9.5
(3)	0.08	-0.04	9.2

2) Formaldehyde

Set	Y(C)	Y(O)	Y(H)	First π I.P. (ev)
(1)	0.00	0.00	0.00	10.9
(2)	0.02	0.04	-0.03	10.6
(3)	0.04	0.08	-0.06	10.3
(4)	0.03	0.06	-0.045	10.4

3) Butadiene (C=C-C=C)
1 2 3 4

Set	Y(C-1)	Y(C-2)	Y(H)	First π I.P. (ev)
(1)	0.04	0.02	-0.02	8.7
(2)	0.08	0.04	-0.04	8.4

4) Glyoxal (O=C-C=O)

Set	Y(O)	Y(C)	Y(H)	First π I.P. (ev)
(1)	0.0	0.0	0.0	10.4
(2)	0.02	0.01	-0.03	10.2
(3)	0.04	0.01	-0.05	9.9
(4)	0.04	-0.01	-0.03	10.1

5) Hexatriene (C=C-C=C-C=C)

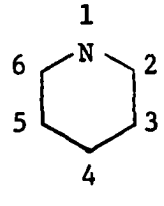
1 2 3 4 5 6

Set	Y(C-1)	Y(C-2)	Y(C-3)	Y(H)	First π I.P. (ev)
(1)	0.00	0.00	0.00	0.00	8.2
(2)	0.04	0.02	0.02	-0.02	8.0
(3)	0.08	0.04	0.04	-0.04	7.7

6) Benzene

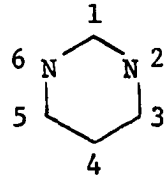
Set	Y(C)	Y(H)	First π I.P. (ev)
(1)	0.00	0.00	9.9
(2)	0.02	-0.02	9.6
(3)	0.04	-0.04	9.3

7) Pyridine



Set	Y(N)	Y(C-2)	Y(C-3)	Y(H)	First π I.P. (ev)
(1)	0.00	0.00	0.00	0.00	9.8
(2)	0.04	0.00	0.02	-0.02	9.6
(3)	0.03	0.015	0.03	-0.03	9.4
(4)	0.02	0.03	0.04	-0.04	9.3

8) 1,3-Diazine

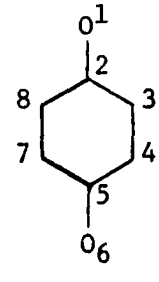


Set	Y(N)	Y(C-1)	Y(C-3)	Y(C-4)	Y(H)	First π I.P. (ev)
(1)	0.00	0.00	0.00	0.00	0.00	9.8
(2)	0.015	0.01	0.01	0.02	-0.02	9.6
(3)	0.03	0.02	0.02	0.04	-0.04	9.4
(4)	0.02	0.02	0.03	0.04	-0.04	9.4

9) 1,4-Diazine

Set	Y(N)	Y(C)	Y(H)	First π I.P. (ev)
(1)	0.00	0.00	0.00	9.8
(2)	0.02	0.01	-0.02	9.6
(3)	0.02	0.03	-0.04	9.4
(4)	0.04	0.02	-0.04	9.5

10) p-Benzoquinone



Set	Y(O)	Y(C-2)	Y(C-3)	Y(H)	First π I.P. (ev)
(1)	0.00	0.00	0.00	0.00	8.5
(2)	0.02	-0.02	0.02	-0.02	8.3
(3)	0.03	-0.03	0.04	-0.04	8.1

a) These results are obtained by SCF-iteration to a self consistency of 0.01 in the bond-order matrix. More iteration steps appear to change the calculated ionization potentials by only ±0.1 ev.

Table 25

A Comparison of Calculated and Experimental First π Ionization Potentials (Y-Set from Table II in Parentheses)

Molecule	Calculated I.P. (ev)	Experimental I.P. (ev)	Difference (ev)
Ethylene (3)	9.2	10.5[a]	1.4
Formaldehyde (4)	10.4	11.8[b]	1.4
Butadiene (2)	8.4	9.2[a]	0.8
Glyoxal (3)	9.9	11.6[c]	1.7
Hexatriene (3)	7.7	8.2[d]	0.5
Benzene (3)	9.3	9.5[a]	0.2
Pyridine (4)	9.3	9.8[e]	0.5
1,3-Diazine (4)	9.4	9.9[e]	0.5
1,4-Diazine (3)	9.4	10.0[e]	0.6
p-Benzoquinone (3)	8.1	9.7-10.0[a]	~1.7

a) Reference 73. p-Benzoquinone I.P. is adiabatic.

b) Reference 74.

c) A value calculated in reference 51.

d) Reference 75. This is an adiabatic ionization potential.

e) Reference 76.

potential was determined by photoelectron spectroscopic measurement, which allows positive identification of the bonding character of the MO from which ionization took place. This work showed that the electron removed in the first ionization of pyridine is removed from a bonding molecular orbital.

The π ionization potentials calculated by Koopmans' theorem are always less than the corresponding experimental values, with the error being between 0.5 and 1.7 ev. These errors are comparable in magnitude to those usually obtained using *ab initio* orbital energies. One wonders why errors of this magnitude occur with *ab initio* calculations and what can be done to improve the theoretical ionization potentials.

There are two areas where errors can be expected to occur. The first is the neglect of electron correlation energy. We have done very approximate Hartree-Fock calculations in the present work, which do not include electron correlation energy. Electron correlation can be expected to increase the ionization potentials to about the same extent as the range of error in the calculations. The second area where error occurs is the neglect of the reorganization of the remaining electrons in the molecule after an electron is ejected. We could include this effect in the mathematical treatment of the theory by doing an open-shell Hartree-Fock calculation[77] on the resulting positive ion. Because an electron has been removed, we would find that the shielding of the nuclei in the molecule by the electrons is diminished and that the orbital exponents of the AO's should be increased. This would allow contraction of the molecular wave function. Another important reorganization of the ion would be shown by such a calculation if the electron were removed from a MO which had greater

electron density on some atoms in the molecule than on others. Excitation from this non-symmetric MO would leave a potential unlike that of the neutral molecule. The result of a hypothetical open shell treatment would be that the electron density of the ion computed with the original MO's of the molecule would change by having electronic charge flow from one atom to another. The energy of the ion would be lowered. We don't have any reliable ways to quantitatively measure the above effects, but we shall attempt some semi-quantitative corrections to the Koopmans' ionization potentials anyway.

If we were to utilize the pair populations method of Hollister and Sinanoğlu[78] to calculate the correlation energy of the neutral molecule and extend their method to include +1 ions, we would find that the molecule has roughly one electron volt more correlation energy than the ion formed by removal of a π-electron. The use of this method to calculate the energy of positive ions has no theoretical justification as the method was developed for closed-shell molecules only. However, the success of the semi-empirical "half-electrons" method of Dewar *et al*[79] in predicting the heats of formation of hydrocarbon radicals provides support for such an extension. With the approximate treatment of Hollister and Sinanoğlu in mind, we shall add 1.5 ev to the Koopmans' theorem ionization potentials to account for the correlation energy change upon removal of a π-electron.

Shown in Table 26 are the results of across-the-board addition of 1.5 ev to the theoretical ionization potentials. The error range of these calculations is from about 0.1 ev to 1.3 ev. This doesn't represent much improvement. The ionization potentials so calculated are now generally

Table 26

A Comparison of Correlation-Corrected First π Ionization Potentials with Experimental Ionization Potentials

Molecule	Corrected I.P. (ev)	Experimental I.P. (ev)	Difference (ev)
Ethylene	10.7	10.5	+0.2
Formaldehyde	11.9	11.8	+0.1
Butadiene	9.9	9.2	+0.7
Glyoxal	11.4	11.6	-0.2
Hexatriene	9.2	8.2	+1.0
Benzene	10.8	9.5	+1.3
Pyridine	10.8	9.8	+1.0
1,3-Diazine	10.9	9.9	+1.0
1,4-Diazine	10.9	10.0	+0.9
p-Benzoquinone	9.6	~9.8	-0.2

too high. We can expect an error in the orbital energies of about $\pm\frac{1}{2}$ ev based upon errors in the approximations made in the MO theory. There is in Table 26 a set of four molecules whose ionization potentials, calculated with Koopmans' ionization potentials plus correlation correction, are within ±0.2 ev of the experimental ionization potentials. Considering the errors expected in the orbital energies, this is excellent agreement. On the other hand, we have a set of six molecules whose ionization potentials calculated using the correlation correction are about one electron volt too large.

To explain the discrepancy exhibited by the molecules of the second group, we need to consider the effect on the ion of electronic reorganization. Any reorganization will lower the energy of the ion and therefore decrease the ionization potential. We could get a qualitative idea of the reorganization due to excitation of an electron from a non-symmetric MO by examining the relative magnitudes of the coefficients of the highest occupied MO (HOMO). But we have no way of estimating the lowering of the ionization potential due to contraction of the ionic wave function relative to the molecular wave function. In a calculation where an atomic basis set is selected and no variation of orbital exponents is allowed in the calculation, it is impossible to account for this effect. We therefore assume that the effect is negligible. This assumption is implicitly made in the "half electrons" method where parameters for the neutral molecule are used to calculate the heats of formation for radicals.

The magnitudes of the expansion coefficients of the HOMO for each of the four molecules whose ionization potentials are nearly correctly predicted in Table 26 are shown in Table 27 as members of Group I. As

Table 27

Magnitudes of the Expansion Coefficients of the Highest Occupied Molecular Orbitals of Several Molecules

Group I: Molecules whose experimental ionization potentials are correctly predicted by the sum of the Koopmans' ionization potential and a correlation correction.

1) **Ethylene:**

C———C

(0.707) (0.707)

2) **Formaldehyde:**

C———O

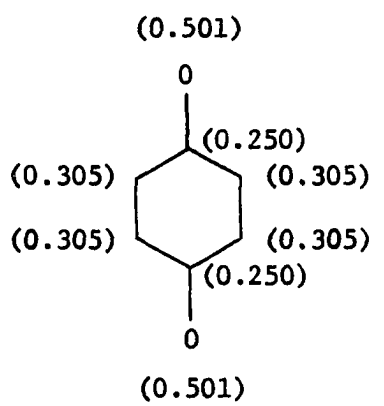
(0.713) (0.701)

3) **Glyoxal:**

O———C———C———O

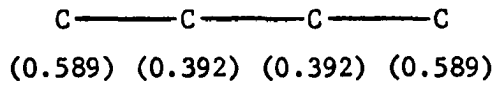
(0.561) (0.430) (0.430) (0.561)

4) **p-Benzoquinone:**

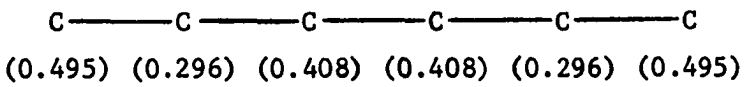


Group II: Molecules whose experimental ionization potentials are not correctly predicted by the sum of the Koopmans' ionization potential and a correlation correction.

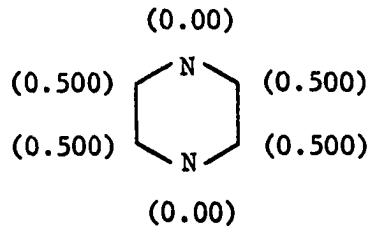
1) Butadiene:



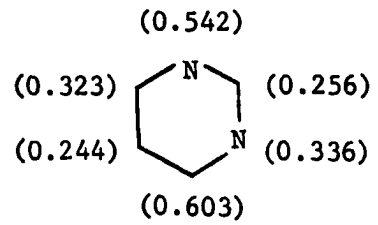
2) Hexatriene:



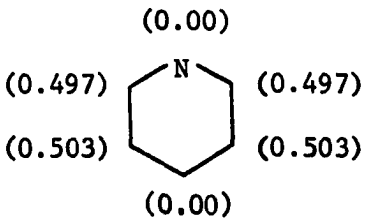
3) 1,4-Diazine:



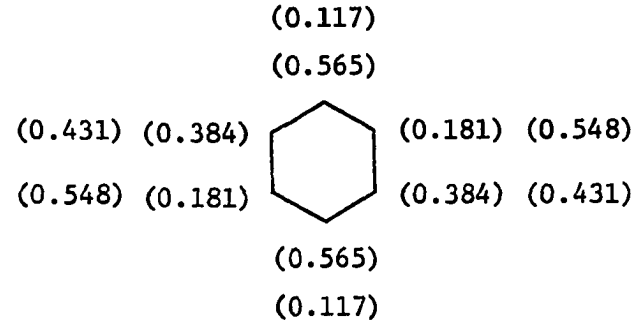
4) 1,3-Diazine:



5) Pyridine:



6) Benzene[a]:



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a) The highest occupied level in benzene is doubly degenerate. The magnitudes of both sets of coefficients are listed. The functions obtained from any linear combination of the coefficients of the degenerate set are legitimate MO's.

expected, the HOMO's of ethylene, formaldehyde, and glyoxal are exactly or very nearly symmetrical. Only p-benzoquinone has a non-symmetrical HOMO. The coefficients of the six-membered ring in p-benzoquinone are nearly equal, but the coefficient of oxygen is double in magnitude the coefficient of its nearest neighbor carbon atom. It is suggested that the reason why electronic charge is not shifted from carbon to oxygen in the ion is the fact that oxygen has only one nearest neighbor, while the carbon in question has three. Since one-center and two-center interactions both go into the determination of a LOAO matrix element, the greater + charge on the oxygen after ionization is offset by the greater number of nearest neighbor interactions seen by the carbon.

The magnitudes of the HOMO coefficients for the six molecules whose Koopmans' ionization potentials plus correlation corrections are in greater error are also shown in Table 27 in Group II. Since the first ionization in benzene is from a set of degenerate MO's, the coefficients of both orbitals are listed. These functions, or any linear combination of them, are legitimate HOMO's. All of the six-membered rings in Table 27 show very unsymmetrical HOMO's. Butadiene and hexatriene have non-symmetrical HOMO's, more so than the HOMO's of the molecules of Group I. Butadiene, with the most symmetrical MO, has the least error, as expected. That the error is greater than that of glyoxal is to be expected from examination of the magnitudes of the coefficients of the HOMO's of both molecules. That the error is so much greater is probably due to errors in the calculated MO orbital energies.

Based upon the examination of the preceding examples, we conclude that the best way to correct the calculated MO orbital energies to produce

reasonably accurate vertical ionization potentials is to add 1.5 ev to Koopmans' ionization potentials for molecules whose HOMO's are either very symmetrical or are such that little reorganization would be expected to occur. For molecules whose HOMO's are not symmetrical, one should add only one-half ev to the negative of the orbital energy. This suggestion produces calculated ionization potentials which agree with the experimental ionization potentials to about ±0.3 ev for the ten examples considered here.

(C) π-π^* Transitions

In order to calculate the vertical π-π^* transition energies with the present theory, we employ the equation suggested by Roothaan[52] for calculating electronic transition energies in molecules

$$E(^{1,3}\bar{\Phi}_{ia}) - E(^{1}\bar{\Phi}_{o}) = \varepsilon_a - \varepsilon_i - (J_{ia} - K_{ia}) \pm K_{ia}, \qquad (111)$$

where $E(^{1,3}\bar{\Phi}_{ia})$ is the energy of the singlet or triplet excited state obtained by promoting an electron from MO i to MO a, $E(^{1}\bar{\Phi}_{o})$ is the energy of the singlet ground state, ε_a is the orbital energy of the MO to which the electron is excited, ε_i is the orbital energy of the MO from which the electron is excited, J_{ia} is the coulomb repulsion integral of an electron in MO i and an electron in MO a, and K_{ia} is the exchange integral over the MO's i and a. The plus sign in equation (111) is to be used in calculating a singlet-singlet transition energy and the minus sign in calculating a singlet-triplet transition energy. In this paper, we are concerned exclusively with singlet-singlet transitions.

The π-π^* transition energies are practically insensitive to the

Y-set chosen to represent the polarization of the σ-core. Therefore, one does not need to specify a Y-set when quoting calculated π-π^* transition energies in molecules.

In Table 28 we list the vertical transition energies calculated with the present *ab initio* MO theory. Transitions are listed only for those cases where experimental data are available for the π-π^* transition energies. Also listed in Table 28 are the errors in the theoretical values relative to the experimental transition energies. With the exception of ethylene, every theoretically computed transition listed in Table 28 differs from the corresponding experimental value by a fairly wide margin. The theoretical results in this table are always too large. This type of behavior is to be expected, as *ab initio* MO calculations of transition energies are always in great error.

Although the semi-empirical MO theories which fit electronic spectra (Pariser-Parr-Pople theory and CNDO/2 as modified by Del Bene and Jaffé) utilize limited configuration interaction (CI), it is not included in the present *ab initio* theory. Limited CI mixes only those states which can be derived from the ground state of the molecule by promoting one electron from one of the computed ground state MO's to another virtual MO. Limited CI has been found necessary to correctly order the transition energies in molecules where there is actual or near degeneracy in the energies of the excited states. The only molecule in Table 28 where limited CI is required is benzene. For this molecule, we have calculated the transition energies with the limited-CI equations of Pariser[80] using the values of β and of the electron-repulsion integrals calculated with the present theory. Although the third π-π^* transition energies calculated with the present theory for

Table 28

A Comparison of Some Calculated π-π^* Transition Energies and Experimental π-π^* Transition Energies

Molecule	Calculated (ev)	Experimental (ev)	Difference (ev)
H_2CO	10.6	8.0[b]	+2.6
Ethylene	7.5	7.6[c]	-0.1
Butadiene	6.7	5.7[b]	+1.0
	8.9	7.2[b]	+1.7
Acrolein	7.8	6.3[d]	+1.5
Glyoxal	9.8	7.6[b]	+2.2
	11.6	9.0[b]	+2.6
Hexatriene	5.8	5.0[d]	+0.8
Benzene	6.4[a]	4.7[e]	+1.7
	7.5[a]	6.1[e]	+1.4
	10.2[a]	6.9[e]	+3.3
p-Benzoquinone	6.8	4.5[b]	+2.3
	7.1	5.1[b]	+2.0

a) After limited CI.

b) Reference 51. The second π-π^* transition of glyoxal is a calculated value.

c) Reference 22, page 58.

d) Reference 81.

e) Reference 11.

butadiene and glyoxal are almost the same as the energies of the second π-π^* transitions, the states derived from these transitions do not mix with one another.[51]

Since the errors in the calculated transition energies appear to be larger for larger transition energies, we plotted these errors against the calculated transition energies. The plot is shown in figure 7. The points on the graph appear to have a low correlation. But, with the exception of the second transition in benzene, the errors in the transition energies for the two molecules which contain rings appear to fall on a line above the errors for linear molecules. The second transition energy has been found difficult to predict by the semi-empirical spectral theories, and a possible reason for their failure is discussed elsewhere.[11]

A recent study reassigning the second and third π-π^* transitions in benzene[82] complicates the problem of calculating the spectra even further. If correct, the reassignment makes all previous limited CI semi-empirical calculations incorrect and puts their parameterization schemes into a bad light. For theoretical calculation of the benzene spectrum, the implication of this reassignment is that very high order CI is necessary even to properly order the excited states with respect to the ground state.

We did a simple least squares fitting of the points in figure 7 by a straight line, using one equation to fit the errors in the ringed compounds and one equation to fit the errors in linear compounds. The resulting equation for benzene and p-benzoquinone errors, denoted by superscript r, is*

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* The second transition of benzene was not included in the least squares fit. This fit is not based on the assignment of the benzene spectrum given in reference 82. Basing the fit on this assignment would not change the equation greatly.

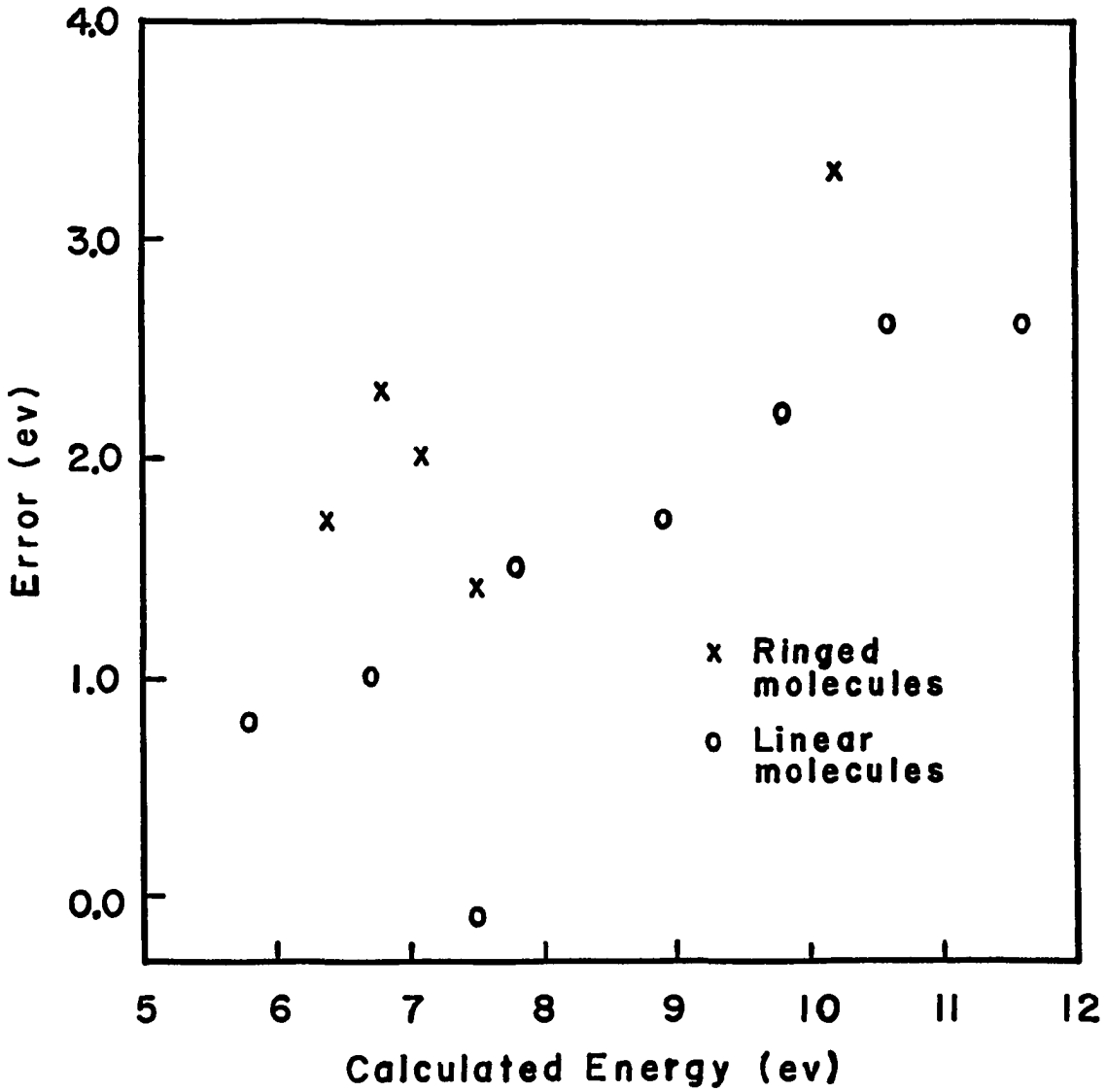


Figure 7

Errors in the calculated π-π^* transition energies in Table 28.

$$\Delta E^{r}\ (ev) \;=\; .38\ \{E^{r}_{calc.}\ (ev)\} - 0.6. \qquad (112)$$

The equation which fits the errors in the spectra of linear molecules (ℓ-superscript) is

$$\Delta E^{\ell}\ (ev) \;=\; 0.29\ \{E^{\ell}_{calc.}\ (ev)\} - 0.9. \qquad (113)$$

We employed these equations to calculate all the errors in the transitions of Table 28 and corrected the calculated transition energies accordingly. These corrected transition energies are compared to the experimental transition energies in Table 29. The errors in the corrected calculations are generally much less than before and within the error limitations of the approximations made in developing the present MO theory. Exceptions to this statement are the second π-π^* transition energy of benzene and, surprisingly, the transition energy of ethylene. Both these transitions are predicted to be of lower energy than they actually are. The benzene transition energy is 0.8 ev too low. This is the same error found in the prediction of this transition energy by the semi-empirical theories.

The error in the ethylene transition energy is very surprising. The transition energy in ethylene computed from equation (111) depends only upon β^{LOAO}_{CC} and upon the one-center and two-center π-π electron-repulsion integrals. We have the corroborating calculation of Cook, Hollis and McWeeny to support our calculation of the non-exchange part of β^{LOAO}_{CC},[36] and the part of β^{LOAO}_{CC} due to σ-π exchange is only about 0.4 ev. It is difficult to see how the large error in the transition energy could result from error in β^{LOAO}_{CC}. The one-center π-π electron repulsions are accurately calculated, and the two-center repulsions are fitted to about

Table 29

Corrected Theoretical π-π^* Transition Energies Compared to Experimental Transition Energies[a]

Molecule	Calculated (ev)	Experimental (ev)	Difference (ev)
H_2CO	8.4	8.0	+0.4
Ethylene	6.2	7.6	-1.4
Butadiene	5.7	5.7	0.0
	7.2	7.2	0.0
Acrolein	6.4	6.3	+0.1
Glyoxal	7.9	7.6	+0.3
	9.1	9.0	+0.1
Hexatriene	5.0	5.0	0.0
Benzene	4.6	4.7	-0.1
	5.3	6.1	-0.8
	6.9	6.9	0.0
p-Benzoquinone	4.8	4.5	+0.3
	5.0	5.1	-0.1

a) References to experimental values are in Table 28.

0.2 ev accuracy by our approximate equation. Perhaps the ethylene case obeys the rule that the simplest member of a series doesn't follow the behavior of the other members.*

The semi-empirical MO theories fit spectra by adjusting the values of the π-π electron-repulsion integrals. What we have done is to suggest an alternative approach, which appears to fit the spectra of the molecules we have considered to about the same accuracy as semi-empirical theories. The simple dependence of the error in the transition energies of the MO calculation upon the calculated energy of the transition may be discussed in CI-language. According to the work of Del Bene and Jaffé,[11] if two states do interact through CI, then the magnitude of that interaction is governed mainly by the energy separation of the two states, the smaller the separation the greater the interaction. This interaction causes the singlet states to repel each other, i.e. their energy separation becomes larger. If we could do infinite-order CI on a molecule, then we would expect the energies of the higher energy excited states considered here to be depressed to a greater extent by interaction with all the states above them than the lower energy excited states. This is the type of behavior shown in the corrections we have made to the calculated transitions.

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* One wonders why ethylene does not conform to the linear plot, while formaldehyde does conform. There is some feeling that the first π-π^* transition of formaldehyde lies not at 8 ev but nearer 11 ev (remark by Lionel Goodman at the 1971 Sanibel Symposium). This would mean that our method predicts formaldehyde accurately, and this removes much of the ethylene mystery.

(D) Effect of Core Polarization upon π MO's

In Table 30, we show the LOAO expansion coefficients produced by the present theory for the MO's of glyoxal. There are four sets of coefficients, one set for each Y-set chosen to represent the polarization of the σ-core. This one example is included to illustrate the effect of core polarization upon the π MO's. The coefficients of the π-MO's are probably the result of a MO calculation most sensitive to charge shifts in the σ-core.

Table 30

π MO's of Glyoxal for Several Sets of the Core Polarization Parameters Y(i)[a]

1) {Y(O), Y(C), Y(H)} = {0.00, 0.00, 0.00}

i	$C_{O_1 i}$	$C_{C_1 i}$	$C_{C_2 i}$	$C_{O_2 i}$	ε_i (au)
1	0.461	0.536	0.536	0.461	-0.478
2	-0.569	-0.420	0.420	0.569	-0.376
3	-0.536	0.461	0.461	-0.536	0.154
4	-0.420	0.569	-0.569	0.420	0.260

2) {Y(O), Y(C), Y(H)} = {0.02, 0.01, -0.03}

i	$C_{O_1 i}$	$C_{C_1 i}$	$C_{C_2 i}$	$C_{O_2 i}$	ε_i (au)
1	0.457	0.540	0.540	0.457	-0.472
2	0.565	0.425	-0.425	-0.565	-0.368
3	-0.540	0.457	0.457	-0.540	0.162
4	0.425	-0.565	0.565	-0.425	0.266

3) {Y(O), Y(C), Y(H)} = {0.04, 0.01, -0.05}

i	$C_{O_1 i}$	$C_{C_1 i}$	$C_{C_2 i}$	$C_{O_2 i}$	ε_i (au)
1	0.452	0.544	0.544	0.452	-0.468
2	0.562	0.430	-0.430	-0.562	-0.362
3	-0.544	0.452	0.452	-0.544	0.167
4	-0.430	0.562	-0.562	0.430	0.270

4) {Y(O), Y(C), Y(H)} = {0.04, -0.01, -0.03}

i	$C_{O_1 i}$	$C_{C_1 i}$	$C_{C_2 i}$	$C_{O_2 i}$	ε_i (au)
1	0.451	0.545	0.545	0.451	-0.472
2	-0.561	-0.430	0.430	0.561	-0.366
3	-0.545	0.451	0.451	-0.545	0.163
4	0.430	-0.561	0.561	-0.430	0.266

a) These results are obtained by SCF-iteration to a self consistency of 0.001 in the bond-order matrix.

CHAPTER VI

A THEORETICAL DISCUSSION OF THE "ONE-ELECTRON" PARAMETERS OF SOME POPULAR NEGLECT OF DIFFERENTIAL OVERLAP SEMI-EMPIRICAL THEORIES

One of the purposes of the development of the present *ab initio* method is to provide a basis for evaluating some of the existing semi-empirical methods. This chapter gives a comparison of some of the semi-empirical parameters to the calculated values of the parameterized quantities. Such a comparison should suggest more accurate ways to obtain the semi-empirical parameters.

(A) Theoretical and Semi-Empirical β's

The β, or resonance integral, for a pair of π atomic orbitals may be defined by the equation

$$\beta_{\mu\nu} = (\mu|V_{core}|\nu), \tag{114}$$

where μ and ν are atomic orbitals, here LOAO's, on the atoms μ and ν. In all-electron calculations, such as the CNDO methods, the V_{core} operator is formally restricted to a sum of the kinetic energy operator and the operators representing the nucleus, π-electron attraction potentials for all the nuclei in the molecule. Generally for π-electron methods, V_{core} includes the above plus the sum of the operators representing the π-electron, σ-core repulsions for all the σ-cores in the molecule. In

Chapter IV, it was found convenient to follow the convention used by the π-electron theories and to include the σ-core operators in V_{core} for this theoretical method.

The effect of the σ-cores upon $\beta_{\mu\nu}$ is slight if μ and ν are LOAO's, the only effect of any magnitude being due to σ-π exchange. By definition, the two-electron integrals are excluded from $\beta_{\mu\nu}$ in CNDO methods, and the σ-π exchange effect is not discussed in theories which treat the π-electrons separately. Accordingly, it is appropriate to compare to the semi-empirical β's that part of β-theoretical which does not include σ-π exchange effects. For molecules with valence σ atomic orbitals which are approximately sp^2 hybridized, the σ-π exchange is only about two-tenths to one-half ev in magnitude.

We calculate the theoretical β for π LOAO's with the equation (Chapter IV)

$$\beta_{\mu\nu}^{LOAO} = S_{\mu\nu}(B_{\mu\nu}^2 \prod_{n\neq\mu,\nu} B_{\mu n} \prod_{m\neq\mu,\nu} B_{\nu m})^{-1} [\{ \prod_{m\neq\mu,\nu} E_{\mu m} \prod_{n\neq\mu,\nu} E_{\nu n}\} K_{\mu\nu} - \sum_{m\neq\mu,\nu} (S_{\mu m} + S_{\nu m}) / 4], \quad (68)$$

where $S_{\mu\nu}$ is the overlap of the AO's μ and ν, $B_{\mu\nu} = (1 - S_{\mu\nu}^2)^{\frac{1}{2}}$, and $E_{\mu m} = \{(1 + B_{\mu m}) / 2\}^{\frac{1}{2}}$. The $K_{\mu\nu}$ are constants which can be obtained from the equation

$$K_{\mu\nu} = -0.112 \{1 + |\xi_\mu - \xi_\nu|\} (\xi_\mu + \xi_\nu) / 2, \quad (65)$$

where ξ are the orbital exponents of the AO's. All the sums Σ in equation (68) are over nearest neighbors to μ and ν only. The products of $B_{\mu n}$ and the products of $E_{\mu m}$ are over nearest-neighbors-to-μ only.

The theoretical β's are identifiable by the superscript LOAO.

If μ and ν have no nearest π-electron bearing neighbors, other than each other, then equation (68) reduces to the form

$$\beta_{\mu\nu}^{LOAO} = S_{\mu\nu} B_{\mu\nu}^{-2} K_{\mu\nu}. \qquad (115)$$

We shall term the β^{LOAO} of equation (115) the local β^{LOAO}. It is the resonance integral in absence of any effects of outside-environment on μ and ν. The $\beta_{\mu\nu}^{LOAO}$ of equation (68) is the environmental $\beta_{\mu\nu}$. It includes the contribution of μ and ν and the contributions of other π-electron bearing atoms in the molecule. Obviously for a two-π-AO system, β^{LOAO} (local) and β^{LOAO} (environmental) become the same.

(1) Evaluation of Environmental Effects and Comparison to Semi-Empirical β's

Table 31 includes $\beta_{\mu\nu}^{LOAO}$ calculated from equation (115), $\beta_{\mu\nu}^{LOAO}$ calculated from equation (68), and the overlaps for "best atom" AO's for the bonded-atom pairs of the π-systems of several molecules. The environmental effect listed in Table 31 is the number of ev which must be added to $\beta_{\mu\nu}^{LOAO}$ (local) to obtain $\beta_{\mu\nu}^{LOAO}$ (environmental). This effect is not small. Its magnitude ranges from about $\frac{1}{2}$ ev to 1 $\frac{1}{2}$ ev, and the effect is such that the magnitude of $\beta_{\mu\nu}^{LOAO}$ (local) is always increased in going to $\beta_{\mu\nu}^{LOAO}$ (environmental).

$\beta_{\mu\nu}^{LOAO}$ (local) is dependent upon $S_{\mu\nu}$. It is not possible to pick a constant term for each atom pair which will accurately reproduce $\beta_{\mu\nu}^{LOAO}$ (local) over a wide range of overlaps. The local part of $\beta_{\mu\nu}^{LOAO}$ should be computed for each case. However, it may be possible to estimate the

Table 31

A Comparison of β^{LOAO} with β's for Three Semi-Empirical Theories[a]

Molecule	Atom Pair	Best Atom AO Overlap	β^{LOAO}[e] (local) (ev)	β^{LOAO}[f] (environmental) (ev)	Environmental Effect (ev)	Slater AO Overlap	β-CNDO[b] (ev)	β-CNDO[c] (ev)	β-P.P.P.[d] (ev)
1,3-Diazine	C, N	0.228	-1.71	-2.58	-0.87	0.215	-4.94	-2.70	-2.576
	C, N	0.233	-1.76	-2.61	-0.85	0.218	-5.01	-2.74	"
	C, N	0.224	-1.69	-2.61	-0.92	0.210	-4.83	-2.64	"
	C, N	0.220	-1.65	-2.58	-0.93	0.205	-4.71	-2.57	"
	C, C	0.260	-1.33	-2.39	-1.06	0.243	-5.10	-2.41	-2.39
	C, C	0.273	-1.41	-2.50	-1.09	0.255	-5.35	-2.53	"
1,4-Diazine	C, N	0.233	-1.76	-2.75	-0.99	0.218	-5.01	-2.74	-2.576
	C, C	0.273	-1.41	-2.45	-1.04	0.255	-5.35	-2.53	-2.39
Ethylene	C, C	0.291	-1.52	-1.52	0.00	0.271	-5.69	-2.69	-2.92
Butadiene	C, C	0.287	-1.50	-2.07	-0.57	0.265	-5.57	-2.63	-2.92
	C, C	0.241	-1.22	-2.39	-1.17	0.220	-4.62	-2.18	-1.68
p-Benzoquinone	C, O	0.224	-2.25	-3.13	-0.88	0.210	-5.46	-3.81	-3.0
	C, C	0.228	-1.15	-2.61	-1.46	0.209	-4.39	-2.07	-1.68
	C, C	0.300	-1.58	-2.72	-1.14	0.280	-5.88	-2.78	-2.92
Acrolein	C, O	0.237	-2.40	-2.88	-0.48	0.223	-5.80	-4.05	-3.0
	C, C	0.237	-1.20	-2.23	-1.03	0.217	-4.56	-2.16	-1.68
	C, C	0.291	-1.52	-2.09	-0.57	0.270	-5.67	-2.68	-2.92
Hexatriene	C, C	0.287	-1.50	-2.07	-0.57	0.265	-5.57	-2.63	-2.92
	C, C	0.241	-1.22	-2.37	-1.15	0.220	-4.62	-2.18	-1.68
Glyoxal	C, O	0.237	-2.40	-2.88	-0.46	0.223	-5.80	-4.05	-3.0
	C, C	0.233	-1.18	-2.07	-0.89	0.213	-4.47	-2.12	-1.68
Pyridine	C, N	0.228	-1.71	-2.67	-0.96	0.215	-4.94	-2.70	-2.576
	C, C	0.269	-1.38	-2.48	-1.10	0.249	-5.23	-2.47	-2.39
	C, C	0.264	-1.35	-2.56	-1.21	0.243	-5.10	-2.41	"
CO	C, O	0.271	-2.80	-2.80	0.00	0.255	-6.63	-4.62	
N_2	N, N	0.292	-1.86	-1.86	0.00	0.282	-7.05	-4.29	
H_2CO	C, O	0.233	-2.37	-2.37	0.00	0.218	-5.67	-3.95	-3.0
Benzene	C, C	0.266	-1.37	-2.56	-1.19	0.245	-5.15	-2.44	-2.39

a) β^{LOAO} is computed without inclusion of σ-π exchange. The CNDO theories shown here ignore this effect.

b) Here β-CNDO is computed from the equation and parameters of reference 8.

c) Here β-CNDO is computed from the equation and parameters of reference 11.

d) All values are taken from reference 83, except β_{CO}, which is from reference 51.

e) Computed using the equation $\beta_{ij}^{LOAO} = (1 - S_{ij}^2)^{-1} (EM)_{i,j}$, where $(EM)_{i,j}$ is the error in the Mulliken approximation for the integral $(i|V_{core}|j)$. Here i and j are π AO's on the atoms i and j.

f) Computed using the full equation for β^{LOAO}, including the environmental effects of nearest neighbors.

environmental effects with reasonable accuracy without using equation (68) for each case. If only one of the members of the μ-ν pair has a nearest neighbor, the environmental effect is about $\frac{1}{2}$ ev. If the μ-ν pair has two nearest neighbors, the environmental effect is about one ev. If there are three nearest neighbors, the effect is about one and one-half ev. One could approximately calculate $\beta_{\mu\nu}^{LOAO}$ by calculating $\beta_{\mu\nu}^{LOAO}$ (local) and increasing the value obtained by one-half ev for each nearest neighbor. For the molecules considered here this procedure produces β^{LOAO}'s accurate to about ±0.2 ev.

Table 31 also includes the overlaps for pairs of Slater atomic functions with orbital exponents determined by Slater's rules (STO's) and the β's for several semi-empirical methods calculated using these overlaps. Both CNDO methods calculate β's with an equation of the general form

$$\beta_{\mu\nu} = \frac{1}{2} \kappa S_{\mu\nu}(\beta_A^\circ + \beta_B^\circ), \tag{116}$$

where κ is a constant, $S_{\mu\nu}$ is the overlap of the STO's μ on atom A and ν on atom B, and β_A° and β_B° are parameters assigned to atoms A and B. The CNDO method of Pople, Santry, and Segal uses κ = 1 for all AO pairs. The CNDO-spectral method of Del Bene and Jaffé[11] employs κ = 0.585 for μ and ν π-AO's and κ = 1 for μ and ν σ-AO's. The two methods differ slightly in their choice of β°'s. The Pariser-Parr-Pople method does not utilize an overlap-dependent formula for β.

The β's computed with the method of Pople, Santry, and Segal are all about two ev greater than the other β's in the table. This discrepancy justifies the choice of κ made by Del Bene and Jaffé for π-β's. The β's

calculated from the method of Del Bene and Jaffé show better agreement with the β's selected in the older Pariser-Parr-Pople scheme. The only major disagreements between the two methods occur in the choices of β_{CO} and in the choice of β_{CC} for the middle π-bond of butadiene. Here there are differences of one-half to one ev.

Although the semi-empirical equation for $\beta_{\mu\nu}$ is very similar to the $\beta_{\mu\nu}^{LOAO}$ (local) equation of the theoretical method, the values calculated for $\beta_{\mu\nu}$ from this equation and reported in Table 31 are all very different from the $\beta_{\mu\nu}^{LOAO}$ (local) results. But the semi-empirical β's of the last two columns of Table 31 are surprisingly similar to the results of the β^{LOAO} (environmental) calculation. They are, in fact, almost identical for the molecules benzene, pyridine, 1,4-diazine and 1,3-diazine, i.e. for those molecules where each atom-pair has two nearest neighbors. The β's of Del Bene and Jaffé agree with the theoretical values except in the cases β_{CO}, β_{CC} for ethylene, β_{NN} for N_2 molecule, and in the qualitative ordering of β_{CC}'s in butadiene. The β's of the Pariser-Parr-Pople scheme agree with the theoretical values except for β_{CC} in ethylene and the β_{CC}'s of butadiene.

The only β where both semi-empirical theories seriously disagree with the theoretical calculations is that for ethylene. Since the LOAO calculations of Cook, Hollis, and McWeeny[36] on ethylene using more time-consuming and more accurate methods corroborate our calculation of β_{CC} for ethylene, we conclude that the semi-empirical β's of Table 31 have no valid theoretical basis in this case.

The more recent semi-empirical MINDO/1 scheme of Baird and Dewar[13] employs a resonance-integral equation which is a slightly modified form

of equation (116). It has the following form:

$$\beta_{\mu\nu} = S_{\mu\nu}(I_{\mu}^{A} + I_{\nu}^{B})\ f(R_{AB}), \tag{117}$$

where

$$f(R_{AB}) = \beta_{CC}^{I} + (\beta_{CC}^{II} / R_{AB}^{2}). \tag{118}$$

Here $S_{\mu\nu}$ is the overlap of the STO's μ and ν. I_{μ}^{A} and I_{ν}^{B} are the neutral-atom valence-state ionization potentials, β_{CC}^{I} and β_{CC}^{II} are parameters, and R_{AB} is the internuclear distance in angstrom units.

Although we do not list the results of calculations of β with this equation in Table 31, we calculated the π resonance integral for ethylene using the STO overlap in Table 31 and the parameters of reference 13. This calculation produced a value for β_{CC} in ethylene of about -1.5 ev. This is almost exactly what we obtained from theoretical calculation.

The problem with the MINDO/1-β is that this value for the π resonance integral would also be used for cases such as the end π-bonds of butadiene. Here, environmental effects cause β_{CC}^{LOAO} to be larger than the MINDO/1-β. We can conclude that the MINDO/1-β will probably reproduce the β^{LOAO} (local) results. There is at least consistency between the value calculated from the MINDO/1 equation and the local nature of the MINDO equation. This consistency does not exist for other semi-empirical theories.

The MINDO/2-β is calculated with an equation analagous to equation (117), in which $f(R_{AB})$ is replaced by a constant term.[14] The parameters employed in the equation for the MINDO/2-β were determined by optimization over a wider range of molecules than for MINDO/1. The β_{CC} calculated for the π-bond of ethylene with MINDO/2 parameters is about -2.0 ev. The

MINDO/2-β appears to be a compromise between β (local) and β (environmental).

The general agreement between theoretical and semi-empirical β's in Table 31 is surprising. One might conclude that the semi-empirical formulas, though local in structure, can simulate theoretical calculation including environmental effects for molecules where all AO-pairs have the same number of nearest neighbors. Where the AO-pairs in molecules have different numbers of nearest neighbors, there is greater disagreement between the semi-empirical β's and the theoretical calculations. The best agreement of any two sets of β's in Table 31 occurs between β^{LOAO} (environmental) and the β's of the older Pariser-Parr-Pople theory.

It is possible to find any $\beta_{\mu\nu}^{LOAO}$ (environmental) approximately reproduced, for a given μ-ν pair, in a given semi-empirical theory. However, no single semi-empirical theory follows the theoretical results in all cases. The reason for this is clear. The semi-empircal theories select a local formula for β where an environmental equation should be used.

It is interesting that the developers of semi-empirical theories which include the overlap (such as the extended Hückel method of Hoffmann[15]) use the same overlap-dependent equation for β as do the developers of no-overlap MO theories. The arguments to justify the choice of an overlap-dependent formula for β are the same for overlap theories as for no-overlap theories. In fact, the two theories formally make use of entirely different atomic basis sets. In the overlap theories, an overlapping basis is used, and the rationale of the overlap-dependent form for β makes more sense. In the no-overlap theories, that a β over orthogonal atomic orbitals should be proportional to the overlap of the corresponding AO's has not been correctly justified. Equation (115) of this paper shows that the β over two

orthogonal functions is a linear function of the overlap for small overlaps. This proportionality occurs through the linear proportionality-to-overlap of the error in the Mulliken approximation. The apparent contradiction of the no-overlap β being proportional to the overlap of the corresponding AO's is therefore removed.

(2) Other Approximate Theoretical Formulas

Mulliken, Rieke, and Brown[84] originally proposed a theoretical expression for β for the neglect-of-overlap formalism in the two-AO case. This expression was later used by Pariser and Parr[5,83] to calculate β's for ethylene and benzene. The equation used by Pariser and Parr is

$$\beta_{pq} = H_{pq}^{core} - (S_{pq}/2)\,(H_{pp}^{core} + H_{qq}^{core}), \qquad (119)$$

where H_{pq}^{core} is the matrix element of the p and q π AO's over the core-potential operator. This equation for β_{pq} is precisely what we have termed $(EM)_{p,q}$ the error in the Mulliken approximation for the integral H_{pq}^{core}. It is the same as β_{pq}^{LOAO} except for the normalization factor $(1-S_{pq}^2)^{-1}$. Later work by Parr[22] using LOAO's resulted in the correct modification to include the $(1-S_{pq}^2)^{-1}$ term in the calculation for the two-AO case.

Pariser and Parr calculated a β for ethylene of -2.80 ev and a β for benzene of -2.48 ev. These results are numerically similar to the values chosen for the semi-empirical β's in the Pariser-Parr-Pople scheme (Table 31). The value for benzene is very nearly the same as that calculated with the present method. The magnitude of the β computed for ethylene is about 1.3 ev greater than the value we have obtained. The papers in which Pariser and Parr did the calculation are not sufficiently detailed to permit critical appraisal. In view of the agreement of the

present method, the studies of Cook, Hollis, and McWeeny, and the recent MINDO method on a value for β-ethylene of about -1.5 ev, the calculated value of -2.80 ev appears doubtful.

The studies of Cook, Hollis, and McWeeny involved computation of LOAO matrix elements from the binomial theorem expansion for the LOAO's proposed originally by Löwdin.[18] These authors suggested an approximate expression for β_{ij}^{LOAO}, as follows:

$$\bar{\beta}_{ij} \simeq \beta_{ij} - \frac{1}{2} S_{ij}(\alpha_i + \alpha_j). \tag{120}$$

This form is based upon keeping terms in the binomial expansion to the first power of overlap only. In this expression, a quantity with a bar refers to LOAO's. Unbarred quantities refer to AO's.

This expression is the same as that proposed originally by Mulliken, Rieke, and Brown. It is a β (local) and neglects the normalization factor $(1 - S_{ij}^2)^{-1}$. For π-electron theory, where overlaps are small, the neglect of this factor causes little error. For σ atomic orbitals, the overlaps are larger, and the neglect of the $(1 - S_{ij}^2)^{-1}$ term is unjustified. Cook, Hollis, and McWeeny did not report any calculations attempted with this approximate equation.

Another approach to the calculation of β for NDO theories is that proposed by Linderberg[38] and discussed in Chapter I of this disseration. The equation proposed by Linderberg is

$$\beta_{\mu\nu} = \frac{1}{R_{\mu\nu}} \frac{d S_{\mu\nu}}{d R_{\mu\nu}} . \tag{11}$$

A graph of $\beta_{\mu\nu}$ computed for the H_2 molecule with this equation

(for 1s orbitals with $\xi = 1.00$) is shown in figure 8. Also shown in figure 8 are the results of calculation with the exact equation for $\beta_{\mu\nu}^{LOAO}$. In view of the obvious conclusion to be drawn from this comparison, it is suggested that the Linderberg equation is unreliable. In figure 8, we also show the results obtained with our approximate equation for $\beta_{\mu\nu}^{LOAO}$, valid for overlaps less than 0.500.

(B) Theoretical and Semi-Empirical One-Center Integrals

The one-center integral for an atomic orbital, which we shall term α, is defined by the equation

$$\alpha_\mu = (\mu|V_{core}|\mu). \tag{121}$$

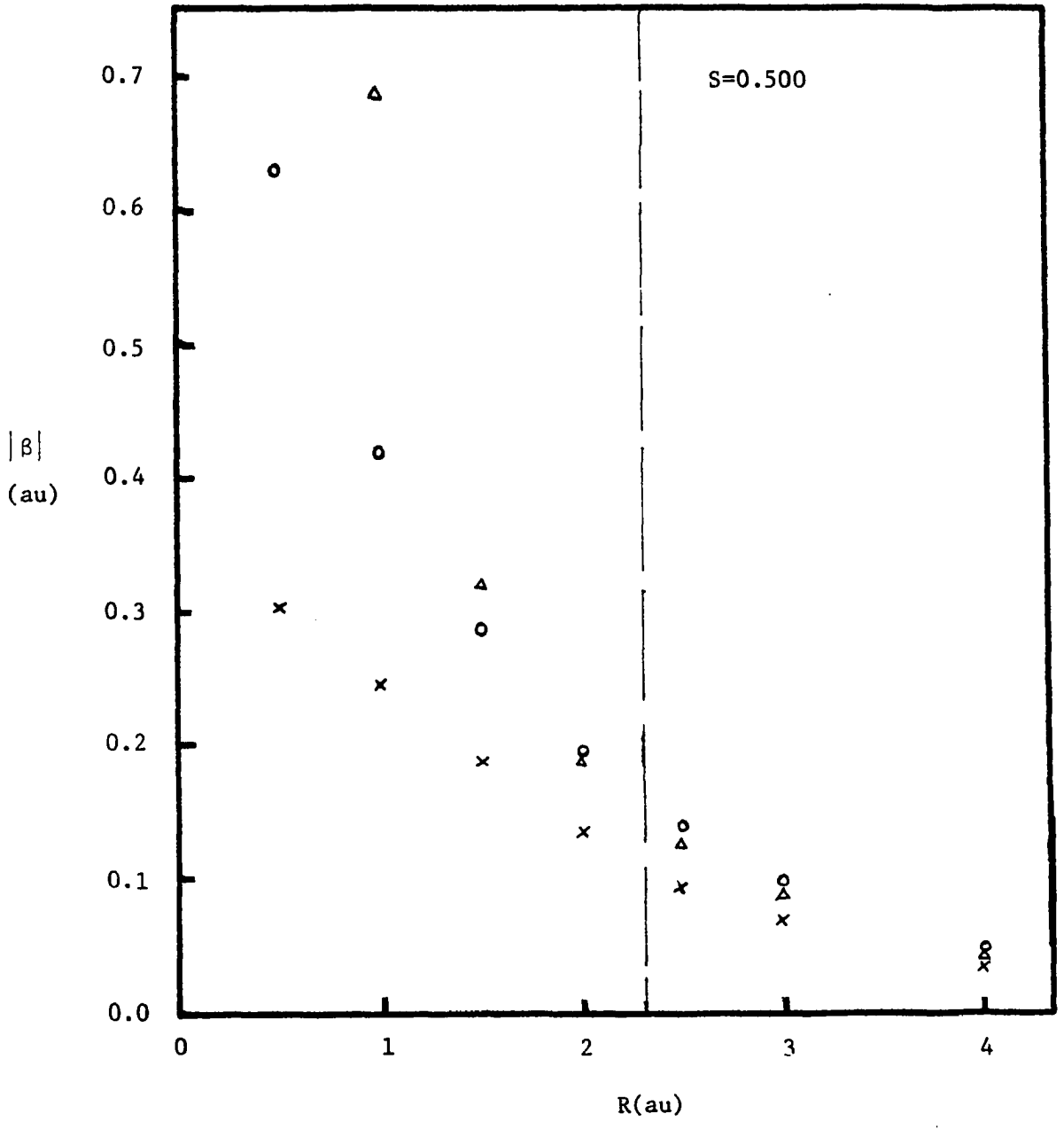
In the present theory μ is a π orbital, and V_{core} is defined in the same way as in the previous section. Since this definition includes the σ-core of electrons in V_{core}, α_μ is not, strictly speaking, a one-electron integral. The two-electron integrals representing the interaction of a π-electron with the σ-core are included in α_μ. These integrals have been qualitatively treated as recommended in reference 36, and a discussion of this treatment is found in Chapter IV.

As pointed out earlier, the π atomic orbitals employed in the present theoretical method are approximate LOAO's. To distinguish the theoretical α_μ, calculated with these functions, we add a LOAO superscript. α_μ^{LOAO} may be calculated from the equation (Chapter IV)

$$\alpha_\mu^{LOAO} = \Big(\prod_{n\neq\mu} B_{\mu n}\Big)^{-2} \Big[\Big\{\Big(\prod_{n\neq\mu} E_{\mu n}^2\Big) - \sum_{n\neq\mu}\Big(\prod_{m\neq n,\mu} E_{\mu m}^2\Big) S_{\mu n}^2/2\Big\} (V_\mu)_{local}$$

Figure 8

H_2 β's from the Exact Method (o), the Linderberg Method (x), and the Method of Chapter IV (Δ).



$$+ \sum_{n\neq\mu} \{(\prod_{m\neq n,\mu} E_{\mu m}^2) S_{\mu n}^2 \{1/2E_{\mu n}^2) - 1\} / 2\} (V_n)_{local}$$

$$- \sum_{n\neq\mu} (\prod_{m\neq n,\mu} E_{\mu m}^2) S_{\mu n}^2 K_{\mu n}] + (V_\mu)_{remote}. \qquad (104)$$

The terms $B_{\mu n}$, $E_{\mu n}$, and $K_{\mu n}$ have been defined earlier, and the limits of the sums and products are set in the discussion following equation (68). All terms on the right-hand side of equation (104) are computed over members of the overlapping atomic orbital set. $(V_\mu)_{local}$ includes the interaction of the μ π-electron with its own core and the cores of its nearest π-electron-bearing neighbors in the molecule. This can be expressed as

$$(V_\mu)_{local} = (\mu|(V_{core})_{local}|\mu), \qquad (102)$$

where the V_{core} operator of equation (9) has been separated into a local part and a part remote relative to μ. Likewise, we can express $(V_\mu)_{remote}$ as

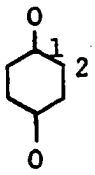
$$(V_\mu)_{remote} = (\mu|(V_{core})_{remote}|\mu), \qquad (122)$$

where $(V_{core})_{remote}$ includes the operators representing the π-core attractions of all non-nearest neighbors which have π-electrons and the π-core attractions of all non-π-electron-bearing neighbors. The methods employed to calculate $(V_\mu)_{local}$ and $(V_\mu)_{remote}$ are discussed in Chapter IV.

By equation (104), the $(V_\mu)_{local}$ is coupled to the $(V)_{local}$'s of the nearest neighbors of μ. This coupling takes place through the overlapping of the AO μ with its nearest neighbors. The results in Table 32

Table 32

The Effect of Overlap-Coupling on $(V_\mu)_{local}$ for Glyoxal and p-Benzoquinone

Molecule	Atom(μ)	$(V_\mu)_{local}$(ev)[a]	$(\alpha_\mu^{LOAO}-(V_\mu)_{remote})$(ev)[b]	Difference(ev)
Glyoxal	C	-29.58	-28.74	0.84
	O	-26.02	-25.40	0.62
p-Benzoquinone	O	-25.65	-24.99	0.66
	C_1	-37.92	-37.05	0.87
	C_2	-28.94	-27.94	1.00

a) $(V_\mu)_{local}$ is the attractive interaction of a π-electron on the atom μ with the core of μ and the cores of μ's nearest π-electron bearing neighbors.

b) α_μ^{LOAO} is defined by $\alpha_\mu^{LOAO} = (\mu|V_{core}|\mu)$, where μ is a LOAO and V_{core} is the operator which includes all cores in the molecule. $(V_\mu)_{remote}$ is the attractive interaction of a π-electron on μ with the cores of non-nearest neighbor, π-bearing atoms and with the cores of atoms which are not a part of the π-electron system.

illustrate quantitatively the effect of this coupling upon $(V_\mu)_{local}$. In Table 32, we have listed, for the molecules glyoxal and p-benzoquinone, the $(V_\mu)_{local}$ and the results of calculation with that part of equation (104) which does not include $(V_\mu)_{remote}$. These calculations were carried out with no σ-core polarization in the molecules. $(V_\mu)_{local}$ is reduced by overlap-coupling in each case of Table 32. This reduction of $(V_\mu)_{local}$ occurs generally.

The CNDO-spectral method of Del Bene and Jaffé and the MINDO method are both modifications of the CNDO/2 method of Pople. The development of a CNDC/2 method was found to be necessary because the original CNDO/1 consistently overestimated the binding energies and underestimated the bond lengths of diatomic molecules. Pople placed the blame for these errors upon the inclusion of the "penetration" effect, the attraction felt by an electron due to the presence of other neutral atoms in the molecule. Such attractions were neglected in CNDO/2, and the justification for this neglect was based upon an examination of the H_2^+ molecule. In this case, the neglect of overlap was found to introduce errors of a similar kind but of opposite sign to the neglect of penetration.

Since CNDO/2 has been so widely extended by other workers, it would appear helpful to have a fuller understanding of the success brought about by dropping the penetration terms. At least for π-electron theory, the one-center integrals over AO's are decreased about one-half to one and one-half ev due to overlap coupling. If this decrease is neglected and the calculations carried out as in CNDO/1, the one-center integrals are found to be too large. Too much binding energy results. If one neglects the overlap-coupling effect and neglects the π-electron, neutral-atom

attractions due to other atoms in the molecule, he qualitatively obtains a better approximation, as in CNDO/2. This is true not only for diatomic π-electron systems, where an atom has only one π-electron bearing nearest neighbor, but also for polyatomic π-electron systems, where an atom may have two or three nearest neighbors. For an atom with several nearest neighbors, equation (104) shows that each neighbor reduces $(V_\mu)_{local}$. Likewise, each neighbor increases the α_μ through the "penetration" effect.

Although CNDO/2 takes account of overlap-coupling in a qualitative manner, we feel that the best policy is to include it quantitatively, as in the present π-electron theory. The overlap-coupling of non-nearest neighbors in the molecule is negligible for π-electron systems, but so is the neutral-atom attraction for a π-electron. For nearest neighbors which do not have π-electrons, there is almost no decrease in $(V_\mu)_{local}$ due to overlap-coupling. At the same time, there is an attraction of the π-electron by the neutral atom. Here, this attraction is not counterbalanced by the overlap-coupling. Therefore, neutral hydrogen atoms increase the π-electron integrals of the atoms to which they are bonded by approximately one-half ev per bonded hydrogen.

Due to the great number of approximations absorbed into the one-center parameters of semi-empirical theories, there is a great deal of apparent "disagreement" among the various theories as to the numerical values selected for the parameters. Therefore, it is not very informative to compare the results of the present method to the semi-empirical one-center terms.

A comparison of the approximate Roothaan matrix elements would be more interesting. The most meaningful case for comparison is that of a

molecule, all of whose atoms are neutral. We consider the CNDO/2 approximation to the Roothaan matrix element $F_{\mu\mu}$ for a carbon $2p\pi$ orbital in the hypothetical case that all atoms in the molecule are neutral. In this case CNDO/2 gives $F_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu)$, where I_μ is the experimental ionization potential and A_μ the experimental electron affinity of the atom. Pople's data for the carbon atom require $F_{\mu\mu}$ to be -5.572 ev.[9] For the cases of ethylene and benzene, with no core polarization, this would be the CNDO/2 carbon π matrix element. With this set of circumstances, we obtain with the theoretical method about -3.3 ev for the matrix element in both cases. Some of the difference of about 2.3 ev could be ascribed to the lack of inclusion of correlation energy in the present theory and the inclusion of this energy in the atomic data of Pople.

(C) Conclusions

In this chapter, we have discussed the theoretical calculation of the integrals computed over the core operator in the π-electron theory. We have compared these calculations to the parameters used in several popular neglect-of-overlap semi-empirical theories. The conclusions drawn from these discussions are as follows:

(1) Both the π-electron resonance integral $\beta_{\mu\nu}$ and the one-center integral α_μ are altered by overlap coupling to nearest neighbors. The $\beta_{\mu\nu}$ is increased in magnitude by overlap-coupling and the α_μ is decreased.

(2) It may be possible to obtain reasonably accurate $\beta_{\mu\nu}$'s (±0.2 ev) by computing $\beta_{\mu\nu}$ locally and then adding one-half ev to $\beta_{\mu\nu}$ (local) for each nearest neighbor. Such a procedure could

not be applied to α_μ.

(3) Semi-empirical equations for $\beta_{\mu\nu}$ are capable of accurately reproducing the theoretical calculations for π-electron systems only where each atom in the molecule has the same number of nearest neighbors.

(4) The need to include overlap-coupling in α_μ has already been recognized in the transition from CNDO/1 to CNDO/2. In CNDO/2 this inclusion is done in qualitatively correct fashion for most AO-pairs but erroneously for a few pairs (non-overlap-coupled pairs).

CHAPTER VII

AN *ab initio* BASIS FOR HÜCKEL THEORY

The Hückel formalism is the simplest computational scheme of all the MO formalisms. The interactions contained in the Hückel Hamiltonian are not treated explicitly. These terms are parameterized. In its simplest form, the Hückel theory is not self-consistent, although more sophisticated Hückel theory provides some self-consistency. Self-consistency, of course, implies that one is approximately including the electronic interactions in an explicit fashion (see reference 4, Chapter 4). It is felt that the simple, non self-consistent Hückel theory is the form worth cultivating. Any attempt to use a self-consistent iteration routine increases the time required to complete the calculation and destroys the most appealing element in Hückel theory. Presently, the Hückel method is the only one fast enough so that calculations on really large molecules are feasible.

At the same time that computational simplicity is the greatest advantage of Hückel theory, it is also its greatest drawback. So little has been made explicit in Hückel theory that we are left trying to make shrewd guesses about the values of the parameters used. The lack of mathematical structure in the parameters makes guessing them very difficult. This difficulty becomes very apparent for heteronuclear molecules. Hückel theory, therefore, removes the computational difficulty but

replaces it with difficulty in evaluating the actual interactions (a kind of conservation-of-difficulty principle). As a result, these interactions are always evaluated by fitting them to experiment.

In this chapter, an attempt will be made to elucidate the parameters by writing some explicit expressions for them. These expressions are in some ways *ad hoc*. They are not derived from first principles but are written to comply with a set of definitions. The results of calculation with these "calculated parameters" will be compared to the results of an *ab initio* CNDO-SCF method and to experiment. This comparison is made for three two-electron molecules. The results of this study have not been successfully extended to larger and more interesting molecules, although the problems associated with such an extension are discussed.

The first step in a study of the Hückel method is to rigorously define the method. (In the literature the method seems to get defined according to what happens to be convenient.) The following set of definitions is essentially that of Parr (reference 22, page 45) and is felt to be mathematically the most precise set of definitions:

(1) The total molecular electronic wave function may be written in the form

$$\psi(x_1, x_2, \ldots) = \prod_i \bar{\Phi}_i(x_i)$$

where Ψ is the total electronic wave function of the molecule, and the $\bar{\Phi}_i$ are molecular spin orbitals. The coordinates of the $i^{\underline{th}}$ electron are x_i. The assumption that the wave function is in this form formally requires that the molecular state be a closed-shell.

(2) The $\bar{\Phi}_i$ are approximated by the LCAO method, where the atomic basis is an orthonormal set. The orthonormal set is assumed here to be a set of LOAO's.

(3) The total electronic energy is given as a sum of the orbital energies. This total electronic energy can be added to the sum of the internuclear repulsions to obtain a total molecular energy which may be compared to experiment.

The first and third parts of the definition define the electrons as independent particles. Statistically, the coordinates of the electrons are random variables; the instantaneous position of an electron is not influenced by the instantaneous positions of the other electrons in the molecule.

One should note that this Ψ, unlike that for SCF theories mentioned in earlier chapters, is not an antisymmetrized function. The function does not automatically obey the Pauli principle; that is, the electrons of the same spin are not forced into different space orbitals by exchange-correlation. This wave function is a correlation-free function. There is no exchange, and there is no correlation of the coulombic type. In order to satisfy the Pauli principle, we shall simply require that the wave function obey this principle. We can enforce this requirement by computing the space orbitals for the molecule and by putting no more than two electrons in each space orbital.

All the correlation effects, both exchange and coulombic will need to be added to the quantities which we calculate with the Hückel method as corrections to the independent-particle model for the electrons. If the corrections are small, it might also be possible to include them in

the matrix elements of the theory. This procedure would be acceptable provided it did not change the calculated charge densities to any great extent.

The second statement in the definition requires that the integrals which appear in the method be evaluated over LOAO's rather than over AO's. The electronic charge densities which are obtained from the calculations are therefore LOAO populations. These populations will agree exactly with AO populations only for homonuclear molecules.

The Hückel formalism defined by these three statements will allow relatively easy calculation of certain observables (total energies and electronic transition energies) but make more difficult the calculation of other observables (ionization potentials and electron affinities). A method based on these definitions will be called a "total energy theory" or a theory of type I.

It should be emphasized that another set of definitions could be agreed upon as defining Hückel theory. Such a set of definitions might be, (1) $\Psi = \det(\Phi_i(x_j))$, (2) the same as the second definition stated previously, and (3) the Hamiltonian is exactly the same as a SCF-NDO Hamiltonian. These definitions would require that Hückel theory is a first approximation to the SCF theories that we have examined in the preceding chapters. These definitions would also require that SCF Hückel theory is exactly the same as the SCF-NDO method. With these definitions, exchange is explicitly included in the method, and the total electronic energy is <u>not</u> given by a sum of orbital energies. Pople[8] appears to implicitly assume these definitions for Hückel theory. With this set of definitions, ionization potentials and electron affinities are easily

calculated, but total electronic energies and electronic transition energies require more calculation. This set of definitions therefore provides a method complementary to the method established by the first set of definitions. A Hückel theory based on these definitions is therefore termed an "ionization potential theory" or a theory of type II.

The two sets of definitions have been explicitly written in an attempt to make this investigation more systematic and to aid in clearing up some confusion about the nature of Hückel theory. (Blyholder and Coulson, for example, seem somewhat confused.[85]) There are, in fact, several Hückel formalisms. The assumptions of Hoffmann[15] imply a different set of definitions than either of the above two sets. His "definitions" are closer to those of a type II theory than to a type I theory. His atomic basis is a set of AO's, however, and the parameters of his method must be interpreted as coming from this basis. His extended Hückel method should be classed as an ionization potential theory. This classification must hold in spite of the fact that Hoffmann uses the method to compute total molecular energies. The energies which he obtains are in great error as they obviously should be.

The purpose of this chapter is to investigate the true independent particle method, that of type I. A method of type I is of great interest in predicting binding energies in molecules. The method of the type II has exactly the same explicit equations for parameters as the CNDO/2 method. There is no need, therefore, to investigate such a method any further.

The three two-electron systems examined in this study are H_2, HeH^+, and LiH (only the valence MO is treated). H_2 is the simplest of the three

and is examined first.

The Roothaan SCF matrix elements for H_2 are, in the NDO formalism

$$F_{11} = (1^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{1}{R_{1H_1}} - \frac{1}{R_{1H_2}}|1^{LOAO}(1)) + \frac{1}{2}(11|11) + (11|22) \quad (122)$$

and

$$F_{12} = (1^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{1}{R_{1H_1}} - \frac{1}{R_{1H_2}}|2^{LOAO}(1)) - \frac{1}{2}(11|22). \quad (123)$$

The atomic basis is a set of two LOAO's generated from the 1s AO's for the two atoms. In the above equations, the atomic orbitals are indicated as $1 = 1s_{H_1}$ and $2 = 1s_{H_2}$. Where LOAO's are explicitly used in the calculation of terms, they are indicated by the superscript LOAO.

The matrix elements of the Hückel theory of the first type may be written

$$\alpha = (1^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{1}{R_{1H_1}} - \frac{1}{R_{1H_2}}|1^{LOAO}(1)) + \frac{1}{4}(11|11) + \frac{1}{4}(11|22) \quad (124)$$

and

$$\beta = (1^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{1}{R_{1H_1}} - \frac{1}{R_{1H_2}}|2^{LOAO}(1)). \quad (125)$$

Definitions of specific terms in α and β are the same as for the SCF method. Equations (124) and (125) are fabricated to fit the type I definitions and to give the electronic transition energy as a difference of orbital energies.

The molecular orbitals for this problem are determined by symmetry. Both the SCF and Hückel methods give the same sets of expansion coefficients. We are interested, therefore, not in the MO's but in the

calculated total energy, ionization potential and electronic transition energy.

The orbital energy of the ground-state MO is termed ε_1 and that of the first excited MO ε_2. In the SCF method, the total electronic energy is given by the equation

$$E^{el}_{total} = 2\varepsilon_1 - \frac{1}{2}\{(11|11) + (11|22)\}, \tag{126}$$

where

$$\varepsilon_1 = F_{11} + F_{12}.$$

The total energy is not a sum of orbital energies. The singlet-singlet electronic transition may be computed by applying equation (111),

$$\Delta E^{1,1} = \varepsilon_2 - \varepsilon_1 - (J_{12} - K_{12}) + K_{12}, \tag{127}$$

where (in the NDO approximation)

$$J_{12} = \frac{1}{2}\{(11|11) + (11|22)\}$$

and

$$K_{12} = \frac{1}{2}\{(11|11) - (11|22)\}.$$

Consider the first three terms of equation (127). Substitution of the orbital energies $\varepsilon_2 = F_{11} - F_{12}$ and $\varepsilon_1 = F_{11} + F_{12}$, and of the equations for J_{12} and K_{12} in terms of the AO repulsion-integrals gives

$$\varepsilon_2 - \varepsilon_1 - (J_{12} - K_{12}) = 2(1^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{1}{R_{1H_1}} - \frac{1}{R_{1H_2}}|2^{LOAO}(1)). \tag{128}$$

The term on the right-hand side of this equation is just 2β (β defined in equation (125)). The SCF singlet-singlet transition is thus

$$\Delta E^{1,1} = 2\beta + K_{12}. \tag{129}$$

The singlet-triplet transition energy is

$$\Delta E^{1,3} = 2\beta - K_{12}. \tag{130}$$

The center of gravity of these two transitions is 2β. This center-of-gravity transition will be indicated by ΔE.

Although the E^{el}_{total} and ΔE's require some calculation beyond computation of the orbital energies, the ionization potential is easily obtained in the SCF method by Koopmans' theorem. The ionization potential is approximated as the negative of the orbital energy ε_1. Therefore one can write

$$I.P. = -\varepsilon_1. \tag{131}$$

With the Hückel method defined by equations (124) and (125), the total electronic energy may be written

$$E^{el}_{total} = 2\varepsilon_1^{Hü} = 2(\alpha + \beta). \tag{132}$$

It should be noted that E_{total} for the molecule is given by the equation

$$E_{total} = E^{el}_{total} + \frac{1}{R_{12}}, \tag{133}$$

where R_{12} is the internuclear distance.

The electronic transition energy is just

$$\Delta E = \varepsilon_2^{Hü} - \varepsilon_1^{Hü} = 2\beta. \tag{134}$$

Since the Hückel theory has an exchangeless wave function, we cannot predict the singlet-triplet split without calculating K_{12} explicitly. The Hückel method can predict only the center of gravity of the first electronic

transition.

Although the total energy and the transition energy are predicted directly from the Hückel orbital energies, the calculation of the ionization potential is more difficult. The ionization potential cannot be predicted by application of Koopmans' theorem. The ionization potential can be calculated from the equation

$$\text{I.P.} = -\epsilon_1^{H\ddot{u}} - \frac{1}{4}\{(11|11) + (11|22)\}. \qquad (135)$$

The LOAO's for H_2 are

$$1^{LOAO} = 1.373\ (1) - 0.615\ (2)$$

and

$$2^{LOAO} = 1.373\ (2) - 0.615\ (1),$$

where the orbital exponents of 1 and 2 are 1.00, and the internuclear distance is 1.42 au. The AO overlap is 0.747. The LOAO's defined by these equations are used to compute the one-electron integrals in the matrix elements of both the SCF and Hückel methods.

The results of calculation of E_{total}, the ΔE's, and the I.P., plus the matrix elements of both methods, are shown in Table 33 together with the experimental quantities. The calculated E_{total}, ΔE, and I.P. are the same for SCF and Hückel methods. The calculated values for these quantities do not agree with experiment. They should not agree since (1) coulombic correlation energy is neglected and (2) the basis set of atomic functions is too small. A minimal basis set calculation on H_2 which explicitly includes the overlap and which uses no integral approximations predicts a binding energy of -2.65 ev (reference 22, page 14) and a singlet-singlet

Table 33

SCF and Hückel Results for H_2 Molecule

	SCF (ev)	Hückel (ev)	Experimental (ev)
E_{total}	-30.07	-30.07	-31.94[a]
Binding energy	- 2.89	- 2.89	- 4.75[a]
$\Delta E^{1,1}$	18.4	-----	~11.8[b]
ΔE	16.7	16.7	-----
$\Delta E^{1,3}$	15.0	-----	~11.3[b]
I.P.	16.9	16.9	~15.5[b]
1,1 matrix element	- 1.78	-16.26	-----
1,2 matrix element	-15.16	- 8.35	-----

a) Reference 86.

b) Reference 55, page 484.

electronic transition energy of about 19 ev (reference 53, page 69). The large errors in the prediction of experimental observables by computation are not due to the approximations that we have made in using the NDO formalism, but to the two effects mentioned above.

It is well known that variation of the orbital exponent gives a better binding energy in H_2. An orbital exponent of about 1.2 gives a calculated binding energy of about -3.5 ev. Could variation of the orbital exponent not also improve the calculated transition energy and ionization potential? ΔE and the I.P. were computed, in the Hückel method, as a function of orbital exponent. The results of this study are shown in Table 34. They show that, while the total molecular energy is worse for orbital exponents less than 1.00, ΔE and the I.P. improve. Although this study suggests some interesting extensions to the calculation of spectra and ionization potentials for larger molecules, such extensions are doomed to failure. Decreasing the orbital exponents of the π-AO's in a π-electron calculation will, in fact, increase the errors in ΔE's and the I.P. This is obvious if one remembers the behavior of β^{LOAO} with changes in overlap (figure 2, Chapter IV).

The H_2 case is rather trivial due to the symmetry. HeH^+ is much more interesting. One would like to define α_H, α_{He}, and β for the Hückel theory so that they are analagous to the quantities defined for H_2.

In the NDO formalism, the Roothaan SCF matrix elements may be written

$$F_{HH} = \left(H^{LOAO}(1)\left|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{He}}{R_{1He}}\right| H^{LOAO}(1)\right) + \frac{1}{2} P_{HH}^{LOAO} (HH|HH) + P_{HeHe}^{LOAO} (HH|HeHe), \quad (136)$$

Table 34

Limited Basis Set Hückel Calculations on H_2 Molecule for Several Values of the Orbital Exponent[a]

Orbital Exponent	Binding energy (ev)	ΔE (ev)	I.P. (ev)
1.2	-3.72	19.9	16.5
1.0	-2.89	16.7	16.9
0.9	-1.41	14.5	16.8
0.8	+0.65	12.5	16.5
Experimental	4.75	-11.6	-15.5

a) Calculations are at R = 1.42 au.

$$F_{HeHe} = (He^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{He}}{R_{1He}}|He^{LOAO}(1))$$

$$+ \frac{1}{2} P_{HeHe}^{LOAO} (HeHe|HeHe) + P_{HH}^{LOAO} (HH|HeHe), \quad (137)$$

and

$$F_{HeH} = (H^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{He}}{R_{1He}}|He^{LOAO}(1)) - \frac{1}{2} P_{HeH}^{LOAO} (HH|HeHe). \quad (138)$$

These matrix elements are written for a limited basis set where H^{LOAO} is the LOAO chiefly centered on the hydrogen atom, He^{LOAO} is the LOAO chiefly centered on the helium atom, and H and He are the corresponding 1s AO's. The P_{ij}^{LOAO} are elements of the LOAO bond-order matrix.

For the Hückel matrix elements, one should choose

$$\alpha_H = (H^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{He}}{R_{1He}}|H^{LOAO}(1))$$

$$+ \frac{1}{4} P_{HH}^{LOAO} (HH|HH) + \frac{1}{4} P_{HeHe}^{LOAO} (HH|HeHe), \quad (139)$$

$$\alpha_{He} = (He^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{He}}{R_{1He}}|He^{LOAO}(1))$$

$$+ \frac{1}{4} P_{HeHe}^{LOAO} (HeHe|HeHe) + \frac{1}{4} P_{HH}^{LOAO} (HH|HeHe), \quad (140)$$

and

$$\beta = (H^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{He}}{R_{1He}}|He^{LOAO}(1)). \quad (141)$$

If we were treating a simple homonuclear molecule, say H_2, then these equations would reduce to equations (124) and (125).

The SCF and Hückel equations for E_{total}^{el}, E_{total}, ΔE, and the I.P. are,

in this example, analagous to the equations for H_2. In the SCF method, E^{el}_{total} is given by a sum of the orbital energies minus the electron repulsions, E_{total} is a sum of E^{el}_{total} and the internuclear repulsion, ΔE is given by equation (111), and the I.P. is approximated as the negative of the orbital energy. In the Hückel method, E^{el}_{total} is a sum of orbital energies, E_{total} is defined the same way as for the SCF method, ΔE is given by a difference in orbital energies and the I.P. is approximated by the negative of the orbital energy minus one-half the electron repulsions felt by the electron in the orbital.

The AO basis chosen for HeH^+ is that determined variationally by Coulson and Duncanson.[54] It is a minimal set with an orbital exponent of 0.722 for $1s_H$ and an exponent of 1.87 for $1s_{He}$. The internuclear distance used in this calculation is that chosen by Coulson, 1.48 au. The overlap of the AO's is 0.484.

LOAO's were calculated using the method shown in Chapter III, and the diagonal elements of the LOAO bond-order matrix were calculated from the AO coefficients of Coulson (see Chapter II). The SCF method began the iteration sequence with the LOAO populations produced by this technique, and iterations were carried out to a self-consistency of 0.01 in the LOAO bond-order matrix. The Hückel calculation used the potential determined by the LOAO populations obtained from the Coulson AO coefficients by transformation. The Hückel calculation is not self-consistent. The results of calculations with the SCF and Hückel methods are compared and compared to more accurate calculations in Table 35.

The SCF and Hückel methods agree very closely on every quantity computed except the wave function. The wave function is probably the

Table 35

SCF and Hückel Results for HeH^+

	SCF (ev)	Hückel (ev)	More Accurate Calculation (ev)
E_{total}	-80.6	-80.8	{ -80.8[a] -80.8[b]
Binding energy	- 1.5	- 1.7	{ - 1.72[a] - 1.68[b]
$\Delta E^{1,1}$	38.3	----	31.8 [b]
ΔE	36.0	35.1	----
I.P.	45.5	44.5	
H,H matrix element	- 9.05	-26.78	----
He,He matrix element	-38.69	-55.66	----
Electronic Population on H	0.314	0.179	0.320[c]
Electronic Population on He	1.686	1.821	1.680[c]

a) Reference 87.

b) Reference 88.

c) Mulliken population analysis of the LCAO wave function of reference 54.

quantity most sensitive to changes in the matrix elements. The overestimation of the charge shift from H to He gives the first indication of a problem which will grow much worse for larger molecules.

The close agreement between the E_{total} calculated by the SCF and Hückel methods and the E_{total} calculated by accurate methods is striking. The calculation of Coulson and Duncanson, which the calculations done here should simulate, gave an E_{total} of only 79.2 ev. This amounts to a prediction of no binding in the molecule. The errors caused by taking certain LOAO electron-repulsion integrals equal to AO electron-repulsion integrals and caused by neglecting electron-repulsion integrals involving overlap-charges have given fortuitous agreement with good calculations. If such errors always move the calculation in the direction of a better answer, then we would be very fortunate. It is possible that they do so, since the errors in H_2 gave a better binding energy by ~0.3 ev. The errors here are larger on an absolute scale since the repulsions are larger.

The LiH molecule is a four-electron problem. However, we shall treat it here as a pseudo two-electron problem. In fact, the LiH molecule will be treated in the most naive fashion possible in the following study. Since this is a study of Hückel theory, it is felt to be more in keeping with the "philosophy" of Hückel theory to treat LiH in such a fashion. The calculations are for a limited basis wave function, that is $1s_H$, $1s_{Li}$, and $2s_{Li}$ only. $2p_{Li}$ will not be included since this would require an extension of the basis beyond the simple intuitive basis of atomic Li. Also, the 1s electrons of Li will be treated as occupying a core MO which does not mix with the valence MO and which screens the Li nucleus. The fact that the $1s_{Li}$ and $2s_{Li}$ STO's are non-orthogonal will be ignored. We

therefore have only a 2x2 determinantal problem to solve.

All the levels of approximation that are implied by the previous discussion have been studied by Fischer.[89] This study showed that the wave functions and energies calculated by the naive method (neglect of 1s-2s non-orthogonality and omission of $2p_{Li}$) are in good agreement with the most accurate of the MO calculations suggested in the previous paragraph. Since the wave functions calculated here will be compared to Fischer's calculation at the same level of approximation, the aims of this study can be accurately met by a naive calculation.

The Roothaan SCF matrix elements for LiH in the NDO approximation are

$$F_{LiLi} = (Li^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{Li}}{R_{1Li}}|Li^{LOAO}(1)) + \frac{1}{2}P^{LOAO}_{LiLi}(LiLi|LiLi)$$
$$+ P^{LOAO}_{HH}(LiLi|HH) + P_{1s_{Li}1s_{Li}}(LiLi|1s_{Li}1s_{Li}), \quad (142)$$

$$F_{HH} = (H^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{Li}}{R_{1Li}}|H^{LOAO}(1)) + \frac{1}{2}P^{LOAO}_{HH}(HH|HH)$$
$$+ P^{LOAO}_{LiLi}(HH|LiLi) + P_{1s_{Li}1s_{Li}}(HH|1s_{Li}1s_{Li}), \quad (143)$$

and

$$F_{HLi} = (H^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{Li}}{R_{1Li}}|Li^{LOAO}(1)) - \frac{1}{2}P^{LOAO}_{LiH}(HH|LiLi). \quad (144)$$

Here H is the 1s function on the hydrogen atom, Li is the 2s Li function, and LOAO's are distinguished from AO's by a superscript. The AO basis is the same as that used by Fischer.

The matrix elements in the Hückel formalism may be defined in the same fashion as HeH^+, the only difference being the presence of a 1s core on Li. These elements are

$$\alpha_{Li} = (Li^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{Li}}{R_{1Li}}|Li^{LOAO}(1)) + \frac{1}{4}P^{LOAO}_{LiLi}(LiLi|LiLi)$$

$$+ \frac{1}{4}P^{LOAO}_{HH}(LiLi|HH) + (LiLi|1s_{Li}1s_{Li}), \quad (145)$$

$$\alpha_H = (H^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{Li}}{R_{1Li}}|H^{LOAO}(1)) + \frac{1}{4}P^{LOAO}_{HH}(HH|HH)$$

$$+ \frac{1}{4}P^{LOAO}_{LiLi}(HH|LiLi) + (HH|1s_{Li}1s_{Li}), \quad (146)$$

and

$$\beta = (H^{LOAO}(1)|-\frac{1}{2}\nabla_1^2 - \frac{Z_H}{R_{1H}} - \frac{Z_{Li}}{R_{1Li}}|Li^{LOAO}(1)). \quad (147)$$

The LOAO's are computed using the method of Chapter III for the internuclear distance 3.02 au (taken by Fischer as the experimental internuclear distance). The overlap (H|Li) is 0.477. The SCF calculation was initiated with a potential calculated using LOAO populations obtained by the transformation from Fischer's AO coefficients (Chapter II). The iteration was taken to a self-consistency of 0.01 in the bond-order matrix. The Hückel calculation utilized a non self-consistent potential calculated with the LOAO populations obtained from the transformation.

The SCF and Hückel results are compared, and both methods are compared to experiment in Table 36. The terms shown in the table are calculated in a fashion analagous to that for H_2 and HeH^+. The SCF and Hückel

Table 36

SCF and Hückel Results for LiH

	SCF (ev)	Hückel (ev)	Experimental or More Accurate Calculation (ev)
E_{total}	219.9	220.8	219.3[a]
Binding Energy	3.1	4.0	2.5[a]
$\Delta E^{1,1}$	10.6	-----	3.3[b]
ΔE	8.6	9.6	
I.P.	10.3	9.5	~8[b]
Li,Li Matrix Element	-0.14	-17.4	-----
H,H Matrix Element	-5.36	-23.7	-----
Electronic Population on Li	0.64	0.34	0.70[c]
Electronic Population on H	1.36	1.66	1.30[c]

a) Reference 78. The total energy is estimated by a sum of the Hartree-Fock and correlation energies.

b) Reference 90.

c) Mulliken population analysis of the wave function of reference 89.

methods agree to within an electron volt on the computed energies. The wave functions, however, disagree. This is the same trend as was found for HeH^+. It should be mentioned that making the Hückel potential self-consistent gives better agreement with the SCF results. Again the NDO errors give a binding energy which is comparable to the experimental binding energy. The calculated electronic transition energies, however, are not comparable to the experimental result. The primary reason for this discrepancy is the use of a limited atomic basis. The addition of a $2p_{Li}$ function should improve the calculations considerably.

From these calculations on H_2, HeH^+, and LiH, we have learned that it is possible to construct a theory of the first type which reproduces the SCF results exactly for homonuclear molecules. For heteronuclear molecules, the results agree to within about one ev for energy calculations, but the Hückel wave function is unreliable.

For larger molecules, one could construct the Hückel matrix elements by analogy to those for the molecules treated here. The general rules for this construction are (1) to define Hückel β's as strictly one-electron integrals and (2) to define Hückel α's by partitioning the electron repulsions so that, in an electronic interaction between two LOAO's, half the electron repulsion appears in one LOAO matrix element and half in the other.

Since the total wave function is assumed not to be antisymmetric in the Hückel method, no exchange appears in the calculated energies. Correlation energies of both exchange and coulombic type will need to be added to the Hückel results as correction factors. One interesting result from the study of the diatomic molecules is that the NDO errors

"include" the coulombic correlation to a certain extent. It may, therefore, be possible to get good E_{total}'s by adding only an exchange correction.

One problem, however, makes the application of the preceding formalism to many-electron heteronuclear systems very difficult. The Hückel β's are smaller than the off-diagonal SCF matrix elements. On the other hand, the Hückel α's are many times larger than their SCF counterparts. Some experimenting with a set of 2x2 secular equations, with a β of roughly -0.1 au and α's of roughly -5 au, shows that, if the α's are not almost exactly the same, then the calculated charge density is almost entirely on the atom with the larger α. This unpleasant situation occured in a test calculation on the glyoxal molecule.

This problem currently limits any application of the method to homonuclear systems. No calculations have, however, been done on systems of this type since the interesting problem is the heteronuclear one.

APPENDIX I

DERIVATION OF $\beta_{\mu\nu}^{LOAO}$ FOR THE FOUR-CENTER CASES

Case C

To produce a set of approximate LOAO's, one orthogonalizes the AO's ϕ_x and ϕ_y, and one orthogonalizes the AO's ϕ_z and ϕ_w. This produces the LOAO set ϕ_x, ϕ_y, ϕ_z, and ϕ_w. Since ϕ_y and ϕ_z are not orthogonal, it is necessary to orthogonalize them to give ϕ_y' and ϕ_z'. The functions which result are as follows:

$$\phi_x = (1 - S_{xy}^2)^{-\frac{1}{2}} \{E_{xy}\, x - (S_{xy}/2E_{xy})y\},$$

$$\phi_y' = (1 - S_{y'z'}^2)^{-\frac{1}{2}} \{E_{y'z'}\, \phi_y - (S_{y'z'}/2E_{y'z'})\phi_z\},$$

$$\phi_z' = (1 - S_{y'z'}^2)^{-\frac{1}{2}} \{E_{y'z'}\, \phi_z - (S_{y'z'}/2E_{y'z'})\phi_y\},$$

and

$$\phi_w = (1 - S_{zw}^2)^{-\frac{1}{2}} \{E_{zw}\, w - (S_{zw}/2E_{zw})z\}.$$

A prime on a subscript of overlaps and E's means that the primed subscript refers to a LOAO rather than an AO. For a specific example of these functions (the glyoxal molecule) see Option A of Chapter III.

β_{xy}^{LOAO} is derived by putting the AO-expansions of ϕ_x' and ϕ_y' into its defining equation (48). The expansion of this integral allows β_{xy}^{LOAO}

to be written as a sum of four terms, as follows:

$$\beta_{xy}^{LOAO} = \text{Term I} + \text{Term II} + \text{Term III} + \text{Term IV}.$$

The terms are

$$\text{Term I} = (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{y'z'}^2)^{-\frac{1}{2}} E_{xy} E_{y'z'} (x|V_{core}|\phi_y),$$

$$\text{Term II} = -\{(1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{y'z'}^2)^{-\frac{1}{2}} E_{xy} S_{y'z'}/(2E_{y'z'})\} (x|V_{core}|\phi_z),$$

$$\text{Term III} = -\{(1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{y'z'}^2)^{-\frac{1}{2}} E_{y'z'} S_{xy}/(2E_{xy})\} (\phi_y|V_{core}|y),$$

and

$$\text{Term IV} = \{(1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{y'z'}^2)^{-\frac{1}{2}} S_{xy} S_{y'z'}/(4E_{xy} E_{y'z'})\}$$

$$(y|V_{core}|\phi_z).$$

Term I is simplified by expanding ϕ_y in terms of AO's in the integral $(x|V_{core}|\phi_y)$ and setting $S_{xz} = S_{xw} = S_{yw} = 0$. To simplify Term I fully, one needs to approximate $S_{y'z'}$ and $E_{y'z'}$. Expansion of $S_{y'z'}$ in terms of AO's, subject to the approximation $S_{xz} = S_{xw} = S_{yw} = 0$, gives

$$S_{y'z'} = (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{zw}^2)^{-\frac{1}{2}} E_{xy} E_{zw} S_{yz}.$$

A still more approximate form for $S_{y'z'}$ is $S_{y'z'} \simeq S_{yz}$. Where $S_{y'z'}^2$ is compared to unity, the second approximation, $S_{y'z'} \simeq S_{yz}$, will be used. Where $S_{y'z'}$ stands alone, the first approximate form for $S_{y'z'}$ will be used. Term I may then be expressed as

$$\text{Term I} = (1 - S_{xy}^2)^{-1} (1 - S_{yz}^2)^{-\frac{1}{2}} E_{yz} \{E_{xy}^2 (x|V_{core}|y) - (S_{xy}/2) (x|V_{core}|x)\}.$$

To simplify Term II, it is necessary to expand ϕ_z in AO's and to employ the approximation that $(x|V_{core}|z) = (x|V_{core}|w) = 0$. Term II is then approximately zero.

Term III is simplified by expansion of ϕ_y in terms of AO's in the integral $(\phi_y|V_{core}|y)$ and by the approximation $S_{y',z'} = S_{yz}$. Term III may then be written

$$\text{Term III} = (1 - S_{xy}^2)^{-1} (1 - S_{yz}^2)^{-\frac{1}{2}} E_{yz} \{- (S_{xy}/2) (y|V_{core}|y) + (S_{xy}^2/(4E_{xy}^2)) (x|V_{core}|y)\}.$$

Simplification of Term IV requires that ϕ_z be expanded in the integral $(y|V_{core}|\phi_z)$ and that applications of the approximations for $S_{y',z'}$ be made. It is also necessary to set $(y|V_{core}|w) = 0$. With these approximations, Term IV becomes

$$\text{Term IV} = \{(1 - S_{xy}^2)^{-1} (1 - S_{yz}^2)^{-\frac{1}{2}} (1 - S_{zw}^2)^{-1} E_{zw} (S_{xy} S_{yz}/4)\} (y|V_{core}|z).$$

The factor $((1 - S_{zw}^2)^{-1} E_{zw})$ has a value of 1.12 for S_{zw} of 0.250. It is a good approximation to set this factor equal to unity. One then obtains the following equation for Term IV:

$$\text{Term IV} = \{(1 - S_{xy}^2)^{-1} (1 - S_{yz}^2)^{-\frac{1}{2}} (S_{xy} S_{yz}/4)\} (y|V_{core}|z).$$

In this equation, the further approximation that $(y|V_{core}|z) = -1.00$ au is made. Term IV becomes

$$\text{Term IV} = (1 - S_{xy}^2)^{-1} (1 - S_{yz}^2)^{-\frac{1}{2}} (S_{xy} S_{yz}/4).$$

The four terms are added together and algebraically simplified to produce the following expression for β_{xy}^{LOAO}:

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-1} (1 - S_{yz}^2)^{-\frac{1}{2}} [E_{yz} (EM)_{x,y} - S_{yz} S_{xy}/4].$$

The derivation of β_{yz}^{LOAO} from the set of approximate LOAO's used to derive β_{xy}^{LOAO} produces an equation which is overly complicated. Another set of approximate LOAO's can be obtained by first orthogonalizing the AO's Φ_y and Φ_z to produce ϕ_y and ϕ_z. ϕ_y is then orthogonalized to Φ_x and ϕ_z orthogonalized to Φ_w. This is the Option B set of LOAO's of Chapter III. The Option B set of LOAO's produces a fairly simple equation for β_{yz}^{LOAO}. It has been established that the β_{yz}^{LOAO} calculated from Option A LOAO's and that calculated from Option B LOAO's agree to within two-tenths of an ev for the glyoxal molecule. We therefore choose to derive β_{yz}^{LOAO} with the Option B LOAO's. The Option B LOAO's are as follows:

$$\phi_x = (1 - S_{xy'}^2)^{-\frac{1}{2}} \{E_{xy'} x - (S_{xy'}/2E_{xy'})\phi_y\},$$

$$\phi_y' = (1 - S_{xy'}^2)^{-\frac{1}{2}} \{E_{xy'} \phi_y - (S_{xy'}/2E_{xy'})x\},$$

$$\phi_{z'} = (1 - S^2_{z',w})^{-\frac{1}{2}} \{E_{z',w}\, \phi_z - (S_{z',w}/2E_{z',w})w\},$$

and

$$\phi_w = (1 - S^2_{z',w})^{-\frac{1}{2}} \{E_{z',w}\, w - (S_{z',w}/2E_{z',w})\phi_z\}.$$

β^{LOAO}_{yz} is then derived by substitution of $\phi_{y'}$ and $\phi_{z'}$ into the defining equation for β^{LOAO}_{yz}. Simplification of this integral gives β^{LOAO}_{yz} as a sum of four terms,

$$\beta^{LOAO}_{yz} = \text{Term I} + \text{Term II} + \text{Term III} + \text{Term IV},$$

where

$$\text{Term I} = (1 - S^2_{xy',})^{-\frac{1}{2}} (1 - S^2_{z',w})^{-\frac{1}{2}} E_{xy',} E_{z',w} (\phi_y|V_{core}|\phi_z),$$

$$\text{Term II} = -\{(1 - S^2_{xy',})^{-\frac{1}{2}} (1 - S^2_{z',w})^{-\frac{1}{2}} E_{xy',} S_{z',w}/(2E_{z',w})\}$$

$$(\phi_y|V_{core}|w),$$

$$\text{Term III} = -\{(1 - S^2_{xy',})^{-\frac{1}{2}} (1 - S^2_{z',w})^{-\frac{1}{2}} E_{z',w} S_{xy',}/(2E_{xy',})\}$$

$$(x|V_{core}|\phi_z),$$

and

$$\text{Term IV} = \{(1 - S^2_{xy',})^{-\frac{1}{2}} (1 - S^2_{z',w})^{-\frac{1}{2}} S_{xy',} S_{z',w}/(4E_{xy',} E_{z',w})\}$$

$$(x|V_{core}|w).$$

Making consistent use of the approximations already developed, we

reduce these equations to the following approximate expressions:

$$\text{Term I} = (1 - S_{yz}^2)^{-1} (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{zw}^2)^{-\frac{1}{2}} E_{xy} E_{zw} (EM)_{y,z},$$

$$\text{Term II} = - (1 - S_{yz}^2)^{-1} (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{zw}^2)^{-\frac{1}{2}} S_{yz} S_{zw}/4,$$

$$\text{Term III} = - (1 - S_{yz}^2)^{-1} (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{zw}^2)^{-\frac{1}{2}} S_{yz} S_{xy}/4,$$

and

$$\text{Term IV} = 0.$$

When these approximate equations are added and the result simplified algebraically, one obtains

$$\beta_{yz}^{LOAO} = (1 - S_{yz}^2)^{-1} (1 - S_{xy}^2)^{-\frac{1}{2}} (1 - S_{zw}^2)^{-\frac{1}{2}} [E_{xy} E_{zw} (EM)_{y,z} - S_{yz} (S_{zw} + S_{xy})/4].$$

Case D

For the non-linear four-center case, it is necessary to derive only one form for $\beta_{\mu\nu}^{LOAO}$, β_{xy}^{LOAO}. To derive β_{xy}^{LOAO}, a set of LOAO's is produced by orthogonalizing Φ_x and Φ_y to produce ϕ_x and ϕ_y. Next, ϕ_y is orthogonalized to Φ_z to produce ϕ_y' and ϕ_z. Last, ϕ_y' is orthogonalized to Φ_w to give the LOAO pair ϕ_y'' and ϕ_w. The set of approximate LOAO's which results from this process is the set ϕ_x, ϕ_y'', ϕ_z, and ϕ_w.

We derive β_{xy}^{LOAO} in terms of the AO's by substituting the expansions of ϕ_x and ϕ_y'' into the defining equation for β_{xy}^{LOAO}. The procedure followed to obtain an approximate expression for β_{xy}^{LOAO} is the same as

that employed in the linear four-center example. If he wishes, one may check the validity of the following approximate equation for β_{xy}^{LOAO} by using the previously established approximation techniques. For Case D, one obtains

$$\beta_{xy}^{LOAO} = (1 - S_{xy}^2)^{-1} (1 - S_{yw}^2)^{-\frac{1}{2}} (1 - S_{yz}^2)^{-\frac{1}{2}} [E_{yw} E_{yz} (EM)_{x,y} - S_{xy} (S_{yz} + S_{yw})/4].$$

APPENDIX II

DERIVATION OF α_μ^{LOAO} IN THE NON-LINEAR FOUR-CENTER CASE

The basis set of approximate LOAO's for Case D has been described in Appendix I. It will not be discussed here. In this example, there should be two distinct α^{LOAO}'s, α_x^{LOAO} and α_y^{LOAO}. Since the x atom has only one nearest neighbor, α_x^{LOAO} has the same form as found for Case B.

α_y^{LOAO} can be derived by substituting the expansion of ϕ_y'' in terms of AO's into the defining equation for α_μ^{LOAO}. The first step in this derivation produces

$$\alpha_y^{LOAO} = (1 - S_{y''w}^2)^{-1} \{E_{y''w}^2 (\phi_y'|V_{core}|\phi_y') + (S_{y''w}^2/4E_{y''w}^2) (w|V_{core}|w) - S_{y''w} (\phi_y'|V_{core}|w)\}.$$

In this equation, a double-prime on the y-subscript of S or E indicates that the overlap is taken with ϕ_y', i.e. $S_{y''w} = (\phi_y'|w)$.

$S_{y''w}$ and $E_{y''w}$ may be simplified by using approximations developed earlier. We approximate $S_{y''w}$ as

$$S_{y''w} = (1 - S_{y'z}^2)^{-\frac{1}{2}} E_{y'z} S_{y'w},$$

or, approximating $S_{y'w}$ in analagous fashion,

$$S_{y''w} = (1 - S^2_{y',z})^{-\frac{1}{2}} (1 - S^2_{xy})^{-\frac{1}{2}} E_{y',z} E_{xy} S_{yw}.$$

Following the practice established in the derivation of $\beta^{LOAO}_{\mu\nu}$, we approximate $S_{y''w}$ by the second equation where $S_{y''w}$ stands alone. Where $S^2_{y''w}$ is compared to unity, i.e. in terms $(1 - S^2_{y''w})$, the approximation $S_{y''w} = S_{yw}$ will be used. Following this same approach, the approximation $S_{y',z} = S_{yz}$ can be used in the terms $(1 - S^2_{y',z})^{-\frac{1}{2}}$ and $E_{y',z}$ in the above equation. This further approximation allows us to write

$$S_{y''w} = (1 - S^2_{yz})^{-\frac{1}{2}} (1 - S^2_{xy})^{-\frac{1}{2}} E_{yz} E_{xy} S_{yw}.$$

The next step in the expansion of α^{LOAO}_{y} in AO's is to expand the approximate LOAO ϕ_y' in the integrals $(\phi_y'|V_{core}|\phi_y')$ and $(\phi_y'|V_{core}|w)$. The first of these integrals has already been derived in the study of the three-AO example. This derivation required the approximations

$$S_{y',z} = (1 - S^2_{xy})^{-\frac{1}{2}} E_{xy} S_{yz},$$

or (where appropriate)

$$S_{y',z} = S_{yz},$$

and

$$(x|V_{core}|z) = 0.$$

The result of these approximations plus some algebraic simplification was equation (72),

$$(\phi_y'|V_{core}|\phi_y') = (1 - S_{yz}^2)^{-1} (1 - S_{xy}^2)^{-1} \{E_{yz}^2 E_{xy}^2 (y|V_{core}|y)$$

$$+ (E_{yz}^2 S_{xy}^2/4E_{xy}^2) (x|V_{core}|x) + (E_{xy}^2 S_{yz}^2/4E_{yz}^2) (z|V_{core}|z)$$

$$- E_{yz}^2 S_{xy} (x|V_{core}|y) - E_{xy}^2 S_{yz} (y|V_{core}|z)\}.$$

With the approximations that $(z|V_{core}|w) = 0$ and $S_{y'z} = S_{yz}$, the second integral, $(\phi_y'|V_{core}|w)$, may be written

$$(\phi_y'|V_{core}|w) = (1 - S_{yz}^2)^{-\frac{1}{2}} E_{yz} (\phi_y|V_{core}|w).$$

This may be further simplified by expanding ϕ_y in terms of AO's in the integral $(\phi_y|V_{core}|w)$ and then setting $(x|V_{core}|w) = 0$. This procedure produces the following approximate equation for $(\phi_y'|V_{core}|w)$:

$$(\phi_y'|V_{core}|w) = (1 - S_{yz}^2)^{-\frac{1}{2}} (1 - S_{xy}^2)^{-\frac{1}{2}} E_{yz} E_{xy} (y|V_{core}|w).$$

These approximate expressions are then substituted for $S_{y''w}$, $E_{y''w}$, $(\phi_y'|V_{core}|\phi_y')$, and $(\phi_y'|V_{core}|w)$ in the equation for α_y^{LOAO}. When this has been done and the result simplified, one obtains

$$\alpha_y^{LOAO} = (1 - S_{yw}^2)^{-1} (1 - S_{yz}^2)^{-1} (1 - S_{xy}^2)^{-1} \{E_{yz}^2 E_{xy}^2 E_{yw}^2 (y|V_{core}|y)$$

$$+ (E_{yw}^2 E_{yz}^2 S_{xy}^2/4E_{xy}^2) (x|V_{core}|x) + (E_{xy}^2 E_{yw}^2 S_{yz}^2/4E_{yz}^2) (z|V_{core}|z)$$

$$+ (E_{yz}^2 E_{xy}^2 S_{yw}^2/4E_{yw}^2) (w|V_{core}|w) - E_{yw}^2 E_{yz}^2 S_{xy} (x|V_{core}|y)$$

$$- E_{yw}^2 E_{xy}^2 S_{yz} (y|V_{core}|z) - E_{xy}^2 E_{yz}^2 S_{yw} (y|V_{core}|w)\}.$$

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